# Statistical mechanics for computer simulators

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## 1 Who needs statistical mechanics?

The topic of these lecture notes is computer simulation. Computer simulation allows us to study properties of many-particle systems. However, not all properties can be directly measured in a simulation. Conversely, most of the quantities that *can* be measured in a simulation, do not correspond to properties that are measured in real experiments. To give a specific example: in a molecular dynamics simulation of liquid water, we could 'measure' the instantaneous positions and velocities of all molecules in the liquid. However, this kind of information cannot be compared to experimental data, because no real experiments provides us with such detailed information. Rather, a typical experiment measures an *averaged* property. Averaged over a large number of particles and, usually, also averaged over the time of the measurement. If we wish to use computer simulation as the numerical counterpart of experiments, we must know what kind of averages we should aim to compute. In order to explain this, we need to introduce the language of statistical mechanics. In statistical mechanics, we encounter thermodynamic concepts such as temperature and entropy and typical mechanical concepts, such as phase space. Although I have no doubt that the reader has, at one time or another, been introduced to all these concepts, I cannot resist sketching how statistical mechanics is "constructed". The aim of this derivation is to show that there is nothing mysterious about concepts such as phase space, temperature and entropy and many of the other statistical mechanical objects that will appear time and again in the remainder of this book.

## 2 Entropy and temperature

Most computer simulations are based on the assumption that classical mechanics can be used to describe the motions of atoms and molecules. This assumption leads to a great simplification in almost all calculations and it is therefore most fortunate that it is indeed justified in many cases of practical interest. It is therefore somewhat surprising that, in order to *'derive'* the basic laws of statistical mechanics, it easier to use the language of quantum mechanics. I will follow this route of 'least resistance'. In fact, for our derivation, we need only little quantum mechanics. Specifically, we need the fact that a quantum mechanical system can be found occur in different states. For the time being, I limit myself to quantum states that are eigenvectors of the Hamiltonian $H$ of the system (i.e. energy eigenstates). For any such state $|i>$, we have that $H|i> = E_i|i>$, where $E_i$ is the energy of state $|i>$. Most examples discussed in quantum-mechanics textbooks concern systems with only few degrees of freedom (e.g. the one-dimensional harmonic oscillator or a particle in a box). For such systems, the degeneracy of energy levels will be small. However, for the systems that are of interest to statistical mechanics (i.e. systems with $\mathcal{O}(10^{23})$ particles), the degeneracy of energy levels is astronomically large. In what follows, I denote by $\Omega(E, V, N)$ the number of eigenstates with energy $E$ of a system of $N$ particles in a volume $V$. I now express the basic assumption of statistical mechanics as follows: *A system with fixed $N$, $V$ and $E$ is equally likely to be found in any of its $\Omega(E)$ eigenstates.* Much of statistical mechanics follows from this simple (but highly non-trivial) assumption.

To see this, let us first consider a system with total energy $E$ that consists of two weakly interaction sub-systems. In this context, 'weakly interacting' means that the sub-systems can exchange energy but that we can write the total energy of the system as the sum of the energies $E_1$ and $E_2$ of the sub-systems. There are many ways in which we can distribute the total energy over the two sub-systems, such that $E_1+E_2 = E$. For a given choice of $E_1$, the total number of degenerate states of the system is $\Omega_1(E_1) \times \Omega_2(E_2)$. Note that the total number of states is not the *sum* but the *product* of the number of states in the individual systems. In what follows, it is convenient to have a measure of the degeneracy of the sub-systems that is additive. A logical choice is to take the (natural) logarithm of the degeneracy. Hence:

$$\ln \Omega(E_1, E - E_1) = \ln \Omega_1(E_1) + \ln \Omega_2(E - E_1) \tag{1}$$

We assume that sub-systems 1 and 2 can exchange energy. What is the most likely distribution of the energy? We know that *every* energy state of the total system is equally likely. But the number of eigenstates that correspond to a given distribution of the energy over the sub-systems, depends very strongly on the value of $E_1$. We wish to know the most likely value of $E_1$, i.e. the one that maximizes $\ln\Omega(E_1, E - E_1)$. The condition for this maximum is that

$$\left(\frac{\partial \ln\Omega(E_1, E - E_1)}{\partial E_1}\right)_{N,V,E} = 0 \tag{2}$$

or, in other words,

$$\left(\frac{\partial \ln\Omega_1(E_1)}{\partial E_1}\right)_{N_1,V_1} = \left(\frac{\partial \ln\Omega_2(E_2)}{\partial E_2}\right)_{N_2,V_2} . \tag{3}$$

We introduce the shorthand notation

$$\beta(E, V, N) \equiv \left(\frac{\partial \ln\Omega(E, V, N)}{\partial E}\right)_{N,V} . \tag{4}$$

With this definition, we can write Eqn. 3 as

$$\beta(E_1, V_1, N_1) = \beta(E_2, V_2, N_2). \tag{5}$$

Clearly, if initially we put all energy in system 1 (say), there will be energy transfer from system 1 to system 2 until Eqn. 4 is satisfied. From that moment on, there is no net energy flow from one sub-system to the other, and we say that the two sub-systems are in thermal equilibrium. This implies that the condition $\beta(E_1, V_1, N_1) = \beta(E_2, V_2, N_2)$ must be equivalent to the statement that the two sub-systems have the same temperature. When thermal equilibrium is reached, $\ln\Omega$ of the total system is at a maximum. This suggests that $\ln\Omega$ is somehow related to the thermodynamic entropy $S$ of the system. After all, the second law of thermodynamics states that the entropy of a system $N, V$ and $E$ is at its maximum when the system is in thermal equilibrium. There are many ways in which the relation between $\ln\Omega$ and entropy can be established. Here I take the simplest route, i.e. we simple *define* the entropy to be equal to $\ln\Omega$. In fact, for (unfortunate) historical reasons, entropy is not simply equal to $\ln\Omega$, rather we have

$$S(N, V, E) \equiv k_B \ln\Omega(N, V, E) \tag{6}$$

where $k_B$ is Boltzmann's constant which, in S.I. units, has the value 1.380658 $10^{-23}$. With this identification, we see that our assumption that all degenerate eigenstates of a quantum system are equally likely immediately implies that, in thermal equilibrium, the entropy of a system of a composite system is at a maximum. It would be a bit premature to refer to this statement as 'the second law of thermodynamics', as I have not yet demonstrated that the present definition of entropy is, indeed, equivalent to the thermodynamic definition. I simply take an advance on this result.

The next thing to note is that thermal equilibrium between sub-systems 1 and 2 implies that $\beta_1 = \beta_2$. In every day life, we have another way to express the same thing: we say that two bodies that are brought in thermal contact are in equilibrium if their temperatures are the same. This suggests that $\beta$ must be related to the absolute temperature. The thermodynamic definition of temperature is

$$1/T = \left(\frac{\partial S}{\partial E}\right)_{V,N} \tag{7}$$

If we use the same definition here, we find that

$$\beta = 1/(k_B T) \ . \tag{8}$$

## 2.1 System at constant temperature

Now that we have defined temperature, we can consider what happens if we have a system (denoted by $S$) that is in thermal equilibrium with a large "heat-bath"($B$). The total system is closed, i.e. the total energy $E{=}E_B{+}E_S$ is fixed (we assume that the system and the bath are weakly coupled, so that we may ignore their interaction energy). Now suppose that the system $S$ is prepared in a specific state $i$ with energy $E_i$. The bath then has an energy $E_B = E - E_i$ and the degeneracy of the bath is given by $\Omega_B(E - E_i)$. Clearly, the degeneracy of the bath determines the probability $P(E_i)$ to find system $S$ in state $i$.

$$P(E_i) = \frac{\Omega_B(E - E_i)}{\sum_i \Omega_B(E - E_i)} \ . \tag{9}$$

To compute $\Omega_B(E - E_i)$, we expand $\ln \Omega_B(E - E_i)$ around $E_i{=}0$.

$$\ln \Omega_B(E - E_i) = \ln \Omega_B(E) - E_i \frac{\partial \ln \Omega_B(E)}{\partial E} + \mathcal{O}(1/E) \tag{10}$$

or, using Eqns. 6 and 7,

$$\ln \Omega_B(E - E_i) = \ln \Omega_B(E) - E_i/k_B T + \mathcal{O}(1/E) \tag{11}$$

If we insert this result in Eqn. 9, we get

$$P(E_i) = \frac{\exp(-E_i/k_B T)}{\sum_i \exp(-E_i/k_B T)} \tag{12}$$

This is the well-known Boltzmann distribution for a system at temperature $T$. Knowledge of the energy distribution allows us to compute the average energy $< E >$ of the system at the given temperature $T$

$$\begin{aligned} < E > &= \sum_i E_i P(E_i) = \frac{E_i \exp(-E_i/k_B T)}{\sum_i \exp(-E_i/k_B T)} \\ &= -\frac{\partial \ln\left(\sum_i \exp(-E_i/k_B T)\right)}{\partial 1/k_B T} \\ &= -\frac{\partial \ln Q}{\partial 1/k_B T} \ , \end{aligned} \tag{13}$$

where, in the last line, I have defined the partition function $Q$. If we compare Eqn. 13 with the thermodynamic relation

$$E = \frac{\partial F/T}{\partial 1/T} \; ,$$

we see that the Helmholtz free energy $F$ is related to the partition function $Q$:

$$F = -k_B T \ln Q \; . \tag{14}$$

Strictly speaking, $F$ is only fixed up to a constant. Or, what amounts to the same thing, the reference point of the energy can be chosen arbitrarily. In what follows, we can use Eqn. 14 without loss of generality. The relation between the Helmholtz free energy and the partition function is often more convenient to use than the relation between $\ln \Omega$ and the entropy. As a consequence, Eqn. 14 is the "workhorse" of equilibrium statistical mechanics.

## 2.2 Other ensembles

In the previous section, we considered a system that could exchange energy with a large thermal bath. This allowed us to derive the relevant statistical mechanical expressions that describe the behavior of a system of $N$ particles in a volume $V$ at a temperature $T$. As in the case in the case of a system at constant $N$,$V$ and $E$, a system at constant $NVT$ can be found in any one of a very large number of quantum states. Such a collection of states is usually referred to as an *ensemble*. The probability to find the system in any one of these states depends on the external conditions (constant $NVE$ or constant $NVT$). The choice of ensemble depends on the "experimental" conditions that one aims to model: an isolated system will be described with the $NVE$-ensemble (which, for historical reasons, is often called the *micro-canonical ensemble*). A system at fixed volume and temperature will be described by the $NVT$ (or *canonical*) ensemble. But often it is convenient to consider systems at constant pressure, or systems that can exchange particles with a reservoir. For every condition, one can introduce the appropriate ensemble. The procedure is very similar to the "derivation" of the canonical ensemble described above. For instance, consider the situation that a system of $N$ particles can exchange energy and volume with a large reservoir. The probability to find the system in a given state with energy $E_i$ and volume $V_i$ is, as before, determined by the number of realizations $\Omega_B(E_{tot} - E_i, V_{tot} - V_i)$ of the "bath". As before, we expand $\ln \Omega_B$ to first order in $E_i$, and now also in $V_i$. Using

$$\frac{\partial S}{\partial E} = \frac{1}{T}$$

and

$$\frac{\partial S}{\partial V} = \frac{P}{T}$$

we obtain

$$\ln \Omega_B(E_{tot} - E_i, V_{tot} - V_i) = \ln \Omega_B(E_{tot}, V_{tot}) - \frac{E_i + PV_i}{k_B T}$$

And the probability to find the system with volume $V$ is given by

$$\mathcal{P}(V) = \frac{Q_{NVT} \exp(-\beta PV)}{\int_0^\infty dV Q_{NVT} \exp(-\beta PV)} \ . \tag{15}$$

Another ensemble of great practical importance is the constant $\mu VT$ or *grand-canonical* ensemble. As before, we consider a system of volume $V$ in contact with a large reservoir. The system can exchange energy and particles with the reservoir. The probability to find $N$ particles in the system in a state with energy $E_i$ is determined by the number of realizations of the bath $\Omega(E_{tot} - E_i, N_{tot} - N)$. Using

$$\frac{\partial S}{\partial N} = \frac{-\mu}{T}$$

and following the same procedure as before, we find that the probability to find $N$ particles in the system in volume $V$ at temperature $T$, is given by

$$\mathcal{P}(N) = \frac{Q_{NVT} \exp(\beta\mu N)}{\sum_{N=0}^\infty Q_{NVT} \exp(\beta\mu N)} \ . \tag{16}$$

It is obvious that we can use the same procedure to generate a large number of different ensembles. However, the $NVT$, $NPT$ and $\mu VT$ ensembles are by far the most important.

# 3 Fluctuations

We started our discussion of statistical mechanical systems by considering a system of $N$ particles in a volume $V$ with total energy $E$. We noted that such a system can be found in a very large number ($\Omega(N, V, E)$) eigenstates. Subsequently, we considered a system of $N$ particles in a volume $V$ that could exchange energy with a large thermal “bath”. In that case, the probability to find the system in a state with energy $E$ was given by Eqn. 12

$$\mathcal{P}(E) = \frac{\Omega(N, V, E) \exp(-E/k_B T)}{\sum_i \exp(-E_i/k_B T)}$$

using Eqn. 6, we can express $\Omega$ in terms of the entropy $S$ and we find

$$\mathcal{P}(E) \sim \exp(-E/k_B T) \exp(S(N, V, E)/k_B)$$

The most likely energy of the system, $E^*$, is the one for which

$$\left(\frac{\partial S}{\partial E}\right)_{E=E^*} = 1/T \ .$$

Expanding $S$ in a Taylor series in $\Delta E \equiv E - E^*$, we get

$$\ln \mathcal{P}(\Delta E) = c + \frac{1}{2k_B}\left(\frac{\partial^2 S}{\partial E^2}\right)(\Delta E)^2 + \mathcal{O}((\Delta E)^3);. \tag{17}$$

In the limit of large $N$, we can ignore terms of order $\Delta E^3$ and we find

$$\mathcal{P}(\Delta E) = \text{constant} \times \exp\left[\frac{1}{2k_B}\left(\frac{\partial^2 S}{\partial E^2}\right)(\Delta E)^2\right] \tag{18}$$

and, recalling that

$$\left(\frac{\partial^2 S}{\partial E^2}\right) = \frac{-1}{C_V T^2}\ ,$$

we obtain

$$\mathcal{P}(\Delta E) = (2\pi k_B C_V T^2)^{-\frac{1}{2}} \exp - \frac{(\Delta E)^2}{2k_B C_V T^2}\ . \tag{19}$$

From Eqn. 19 we immediately see that the mean-square fluctuation in the energy of a system a constant $N, V, T$ is directly related to the heat capacity $C_V$:

$$< (\Delta E)^2 >= k_B T^2 C_V\ . \tag{20}$$

Using Eqn. 19 we can relate any average in the $NVE$ ensemble to the corresponding average in the $NVT$ ensemble by Taylor expansion:

$$< A >_{NVT} = < A >_{NVE} + \left(\frac{\partial A}{\partial E}\right) < \Delta E > + \frac{1}{2}\left(\frac{\partial^2 A}{\partial E^2}\right) < (\Delta E)^2 > + \mathcal{O}(< \Delta E^3 >) \tag{21}$$

A well-known application of this conversion is the expression derived by Lebowitz, Percus and Verlet for the relation between kinetic energy fluctuations in the $NVE$ and $NVT$ ensembles [6]:

$$< (\Delta K)^2 >_{NVE} = \frac{3Nk_B^2 T^2}{2}\left(1 - \frac{3Nk_B}{2C_V}\right) \tag{22}$$

Of course, one can use a similar approach to relate averages in other ensembles.

## 3.1 Histograms and Landau Free energies

Let us look once more at the probability to find a system with volume $V$ in an $NPT$ ensemble. According to Eqn. 15 this probability is given by

$$\mathcal{P}(V) = c\, Q(N, V, T) \exp(-\beta P_0 V)$$

where $c$ is a normalization constant. We use the notation $P_0$ to distinguish that applied pressure (i.e. the pressure of the reservoir) from $P(N, V, T)$, the pressure of the system. Using the relation between the canonical partition function $Q(N,V,T)$ and the Helmholtz free energy $F(N,V,T)$, we can rewrite Eqn. 15 as

$$\mathcal{P}(V) = c\ \exp[-\beta(F(N,V,T) + P_0 V)]\ . \tag{23}$$

From this equation we see that the probability to find the system in volume $V$ is determined by the behavior of $F + P_0 V$. But this is nothing other than the Gibbs free energy $G$. The most likely volume is the one for which $G$ is at its minimum. This happens when

$$\frac{\partial F(N,V,T)}{\partial V} \equiv -P(N,V,T) = -P_0$$

i.e. when the thermodynamic pressure of the system is equal to the applied pressure. In fact, if we could measure the histogram $\mathcal{P}(V)$, we could directly measure the variation of the Helmholtz free energy with volume. The higher the free energy of a given volume fluctuation, the less likely we are to observe this fluctuation. In principle, we could determine the complete equation of state of the system from knowledge of $\mathcal{P}(V)$. To see this, consider

$$\frac{\partial \ln \mathcal{P}(V)}{\partial V} = \beta(P(N,V,T) - P_0) \tag{24}$$

One amusing consequence of this expression is the relation between two-phase coexistence and van der Waals loops in the equation of state [5]. Suppose that a system at a given pressure $P_0$ undergoes a first-orde phase transition from a state with volume $V_1$ to a state with volume $V_2$. At coexistence, the system is equally likely to be found in either state, but it is unlikely to be in a state with intermediate density. Hence, the histogram of volumes, $\mathcal{P}(V)$ will be double-peaked. Eqn. 24 the immediately shows that the pressure as a function of volume should exhibit an oscillation around $P_0$.

The relation between probabilities of fluctuations and free energies is, in fact, quite general. To see this, let us consider a system with $N$ particles in volume $V$ in contact with a reservoir at constant $T$. Now let us assume that we are not interested in the fluctuations of the energy of the system, but in fluctuations of some other observable property, e.g. the total magnetic moment $M$. We wish to know the probability that the system is found in a state with magnetic moment $M$. To do so, we should sum the probabilities of all states $i$ that satisfy the constraint $M_i$=$M$.

$$\mathcal{P}(M) = \frac{\sum_i \exp(-\beta E_i)\delta_{M_i,M}}{\sum_i \exp(-\beta E_i)}$$

where the Kronecker delta constrains the sum to those terms that have the required magnetic moment. We see that the restricted sum in the numerator has the form of a partition function and we denote it by $Q(N,V,T,M)$. We also define an associated free energy

$$F(N,V,T,M) \equiv -k_B T \ln(Q(N,V,T,M)) \tag{25}$$

We refer to $F(N, V, T, M)$ as the Landau free energy associated with the variable $M$. Clearly, there is a close connection between (Landau) free energies and constraints. We define a subset of all possible states of the system by the constraint $M_i{=}M$. The Landau free energy then determines the probability that the system will spontaneously be found in a state that satisfies this constraint:

$$\mathcal{P}(M) = c \ \exp(-\beta F(N, V, T, M))$$

In computer simulations, we can measure Landau free energies by sampling a histogram of the spontaneous fluctuations of $M$. However, this approach in its naive form is not very useful, as we can only hope to sample fluctuations with an associated Landau free energy of at most a few $k_BT$. If we wish to study the Landau free energy over a wider range, non-standard sampling schemes are needed (see e.g. [77, 7]).

# 4 Classical Statistical Mechanics

Thus far, we have formulated statistical mechanics in purely quantum-mechanical terms. The entropy is related to the density of states of a system with energy $E$, volume $V$ and number of particles $N$. And similarly, the Helmholtz free energy is related to the partition function $Q$, a sum over all quantum states $i$ of the Boltzmann factor $\exp(-E_i/k_BT)$. To be specific, let us consider the average value of some observable $A$. We know the probability that a system at temperature $T$ will be found in an energy eigenstate with energy $E_i$ and we can therefore compute the thermal average of $A$ as

$$< A >= \frac{\sum_i \exp(-E_i/k_BT) < i|A|i >}{\sum_i \exp(-E_i/k_BT)} \,. \tag{26}$$

This equation suggests how we should go about computing thermal averages: first we solve the Schrödinger equation for the (many-body) system of interest, and next we compute the expectation value of the operator $A$ for all those quantum states that have a non-negligible statistical weight. Unfortunately, this approach is doomed for all but the simplest systems. First of all, we cannot hope to solve the Schrödinger equation for an arbitrary many-body. And secondly, even if we could, the number of quantum states that contribute to the average in Eqn. 26 would be so astronomically large ($\mathcal{O}(10^{10^{25}})$) that a numerical evaluation of all expectation values would be unfeasible. Fortunately, Eqn. 26 can be simplified to a more workable expression in the classical limit ($h \to 0$). To this end, we first rewrite Eqn. 26 in a form that is independent of the specific basis set. We note that $\exp(-E_i/k_BT) = < i|\exp(-H/k_BT)|i >$, where $H$ is the Hamiltonian of the system. Using this relation, we can write

$$< A > \ = \ \frac{\sum_i < i|\exp(-H/k_BT)A|i >}{\sum_i < i|\exp(-H/k_BT)|i >}$$

$$= \frac{Tr\exp(-H/k_BT)A}{Tr\exp(-H/k_BT)} \tag{27}$$

where $Tr$ denotes the trace of the operator. As the value of the trace of an operator does not depend on the choice of the basis set, we can compute thermal averages using any basis set we like. Preferably, we use simple basis sets, such as the set of eigenfunctions of the position or the momentum operator. The reason why use of these basis sets may be advantageous can be understood as follows. We recall that the Hamiltonian $H$ is the sum of a kinetic part $K$ and a potential part $U$. The kinetic-energy operator is a quadratic function of the momenta of all particles. As a consequence, momentum eigenstates are also eigenfunctions of the kinetic energy operator. Similarly, the potential energy operator is a function of the particle coordinates. Matrix elements of $U$ are therefore most conveniently computed in a basis set of position eigenfunctions. However, $H = K + U$ itself is not diagonal in either basis set, nor is $\exp(-\beta(K+U))$. However, if we could replace $\exp(-\beta H)$ by $\exp(-\beta K)\exp(-\beta U)$, then we could simplify equation 27 considerably. In general, we cannot make this replacement because

$$\exp(-\beta K)\exp(-\beta U) = \exp(-\beta\left((K+U) + \mathcal{O}([K,U])\right))$$

where $[K,U]$ is the commutator of the kinetic and potential energy operators while $\mathcal{O}([K,U])$ is meant to denote all terms containing commutators and higher-order commutators of $K$ and $U$. It is easy to verify that the commutator $[K,U]$ is of order $\hbar$. Hence, in the limit $\hbar \to 0$, we may ignore the terms of order $\mathcal{O}([K,U])$. In that case, we can write

$$Tr\exp(-\beta H) \approx Tr\exp(-\beta U)\exp(-\beta K) \tag{28}$$

If we use the notation $|r>$ for eigenvectors of the position operator and $|k>$ for eigenvectors of the momentum operator, we can express Eqn. 28 as

$$Tr\exp(-\beta H) = \sum_{r,k} < r|e^{-\beta U}|r >< r|k >< k|e^{-\beta K}|k >< k|r > \tag{29}$$

All matrix elements can be evaluated directly:

$$< r|\exp(-\beta U)|r >= \exp(-\beta U(\mathbf{r}^N))$$

where $U(\mathbf{r}^N)$ on the right hand side is no longer an operator, but a function of the coordinates of all $N$ particles. Similarly,

$$< k|\exp(-\beta K)|k >= \exp(-\beta\sum_{i=1}^{N} p_i^2/(2m_i))$$

where $p_i = \hbar k_i$. And finally,

$$< r|k >< k|r >= 1/V^N$$

where $V$ is the volume of the system and $N$ the number of particles. Finally, we can replace the sum over states by an integration over all coordinates and momenta. The final result is

$$Tr\,\exp(-\beta H) \approx \frac{1}{h^{dN} N!} \int d\mathbf{p}^N d\mathbf{r}^N \exp[-\beta(\sum_i p_i^2/(2m_i) + U(\mathbf{r}^N))] \tag{30}$$

where $d$ is the dimensionality of the system. The factor $1/N!$ is a direct result of the indistinguishability of identical particles. In almost the same way, we can derive the classical limit for $Tr\,\exp(-\beta H)A$ and finally, we can write the classical expression for the thermal average of the observable $A$ as

$$< A >= \frac{\int d\mathbf{p}^N d\mathbf{r}^N \exp[-\beta(\sum_i p_i^2/(2m_i) + U(\mathbf{r}^N))]A(\mathbf{p}^N, \mathbf{q}^N)}{\int d\mathbf{p}^N d\mathbf{r}^N \exp[-\beta(\sum_i p_i^2/(2m_i) + U(\mathbf{r}^N))]} \tag{31}$$

Equations 30 and 31 are the starting point for virtually all classical simulations of many-body systems.

## 4.1 Ergodicity

Thus far, we have discussed the average behavior of many-body systems in a purely static sense: we only introduced the assumption that every quantum state of a many-body system with energy $E$ is equally likely to be occupied. Such an average over all possible quantum states of a system, is called an "ensemble" average. However, this is not the way we usually think about the average behavior of a system. In most experiments we perform a series of measurements during a certain time-interval and then determine the average of these measurements. In fact, the idea behind Molecular Dynamics simulations is precisely that we can study the average behavior of a many-particle system simply by computing the natural time evolution of that system numerically and averaging the quantity of interest over a sufficiently long time. To take a specific example, let us consider a fluid consisting of atoms. Suppose that we wish to compute the average density of the fluid at a distance $r$ from a given atom $i$, $\rho_i(r)$. Clearly, the instantaneous density depends on the coordinates $\mathbf{q}_j$ of all particles $j$ in the system. As time progresses, the atomic coordinates will change (according to Newton's equations of motion), and hence the density around atom $i$ will change. Provided that we have specified the initial coordinates and momenta of all atoms $(\mathbf{q}^N(0), \mathbf{p}^N(0))$ we know, at least in principle, the time evolution of $\rho_i(r; \mathbf{q}^N(0), \mathbf{p}^N(0), t)$. In a Molecular Dynamics simulation, we measure the time-averaged density $\overline{\rho_i(r)}$ of a system of $N$ atoms, in a volume $V$, at a constant total energy $E$:

$$\overline{\rho_i(r)} = \lim_{T\to\infty} \frac{1}{T} \int_0^T dt' \; \rho_i(r; t') \; . \tag{32}$$

Note that, in writing down this equation, we have implicitly assumed that, for $T$ sufficiently long, the time-average does not depend on the initial conditions.

This is, in fact, a subtle assumption that is not true in general (see, *e.g.* ref. [8]). However, we shall disregard subtleties and simply assume that, once we have specified $N$, $V$ and $E$, time-averages do not depend on the initial coordinates and momenta. If that is so, then we would not change our result for $\overline{\rho_i(r)}$ if we average over many different initial conditions, *i.e.* we consider the hypothetical situation where we run a large number of Molecular Dynamics simulations at the same values for $N$, $V$ and $E$, but with different initial coordinates and momenta,

$$\overline{\rho_i(r)} = \frac{\sum\limits_{\text{initial conditions}} \left( \lim_{T\to\infty} \frac{1}{T} \int_0^T dt'\ \rho_i(r; \mathbf{q}^N(0), \mathbf{p}^N(0), t') \right)}{\text{number of initial conditions}} \ . \tag{33}$$

We now consider the limiting case where we average over *all* initial conditions compatible with the imposed values of $N$, $V$ and $E$. In that case, we can replace the sum over initial conditions by an integral

$$\frac{\sum\limits_{\text{initial conditions}} f(\mathbf{q}^N(0), \mathbf{p}^N(0))}{\text{number of initial conditions}} \to \frac{\int_E d\mathbf{q}^N d\mathbf{p}^N f(\mathbf{q}^N(0), \mathbf{p}^N(0))}{\Omega(N,V,E)} \ , \tag{34}$$

where $\Omega(N,V,E) = \int_E d\mathbf{q}^N d\mathbf{p}^N$ (we have ignored a constant factor[1]). The subscript $E$ on the integrals indicates that the integration is restricted to a shell of constant energy $E$. We denote an ensemble average by $\langle \cdots \rangle$, to distinguish it from a time-average, denoted by a bar. If we switch the order of the time-averaging and the averaging over initial conditions, we find

$$\overline{\rho_i(r)} = \lim_{T\to\infty} \frac{1}{T} \int dt'\ \langle \rho_i(r; \mathbf{q}^N(0), \mathbf{p}^N(0), t') \rangle_{NVE} \ . \tag{35}$$

However, the ensemble average in the above equation does not depend on the time $t'$. This is so, because there is a one-to-one correspondence between the initial phase-space coordinates of a system, and those that specify the state of the system at a later time $t'$ (see *e.g.* [9, 8]). Hence, averaging over all initial phase-space coordinates is equivalent to averaging over the time-evolved phase-space coordinates. For this reason, we can leave out the time averaging in Eqn. 35, and we find

$$\overline{\rho_i(r)} = \langle \rho_i(r) \rangle_{NVE} \ . \tag{36}$$

The above equation states that, if we wish to compute the average of a function of the coordinates and momenta of a many-particle system, we can *either* compute that quantity by time-averaging (the 'MD' approach), *or* by ensemble averaging

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[1] If we consider a quantum-mechanical system, then $\Omega(N,V,E)$ is simply the number of quantum states of that system, for given $N$, $V$ and $E$. In the classical limit, the number of quantum states of a $d$-dimensional system of $N$ distinguishable, structureless particles is given by $\Omega(N,V,E) = (\int d\mathbf{p}^N d\mathbf{q}^N)/h^{dN}$. For $N$ *indistinguishable* particles, we should divide the latter expression by a factor $N!$.

(the 'MC' approach). It should be stressed that the preceding paragraphs are only meant to make Eqn. 36 *plausible*, not as a proof. In fact, that would have been quite impossible because Eqn. 36 is not true in general. However, in what follows, we shall simply assume that the 'ergodic hypothesis', as Eqn. 36 is usually referred to, applies to the systems that we study in computer simulations. The reader should, however, be aware that there are many examples of systems that are not ergodic *in practice* (*e.g.* glasses, meta-stable phases) or even *in principle*, *e.g.* nearly harmonic solids.

# 5 The Monte Carlo method

In oder to introduce the Monte Carlo method, we start from the classical expression for the partition function $Q$:

$$Q = c \int \mathrm{d}\mathbf{p}^N \mathrm{d}\mathbf{r}^N \exp[-\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)/k_B T] \ , \tag{37}$$

where $\mathbf{r}^N$ stands for the coordinates of all $N$ particles, and $\mathbf{p}^N$ for the corresponding momenta. The function $\mathcal{H}(\mathbf{q}^N, \mathbf{p}^N)$ is the Hamiltonian of the system. It expresses the total energy of an isolated system as a function of the coordinates and momenta of the constituent particles: $\mathcal{H} = \mathcal{K} + \mathcal{U}$, where $\mathcal{K}$ is the kinetic energy of the system and $\mathcal{U}$ is the potential energy. Finally, $c$ is a constant of proportionality, chosen such that the sum over quantum states in equation (14) approaches the classical partition function in the limit $\hbar \to 0$. For instance, for a system of $N$ identical atoms, $c = 1/(h^{3N}N!)$. The classical equation corresponding to equation (26) is:

$$\langle A \rangle = \frac{\int \mathrm{d}\mathbf{p}^N \mathrm{d}\mathbf{r}^N \ A(\mathbf{p}^N, \mathbf{r}^N) \exp[-\beta\mathcal{H}(\mathbf{p}^N, \mathbf{r}^N)]}{\int \mathrm{d}\mathbf{p}^N \mathrm{d}\mathbf{r}^N \ \exp[-\beta\mathcal{H}(\mathbf{p}^N, \mathbf{r}^N)]} \ , \tag{38}$$

where $\beta = 1/k_B T$. In the above equation, the observable $A$ has been expressed as a function of coordinates and momenta. As $\mathcal{K}$ is a quadratic function of the momenta the integration over momenta can be carried out analytically. Hence, averages of functions that depend on momenta only are usually easy to evaluate (this is not the case when hard constraints are used). The difficult problem is the computation of averages of functions $A(\mathbf{r}^N)$. Only in a few exceptional cases can the multi-dimensional integral over particle coordinates be computed analytically, in all other cases numerical techniques must be used.

Having thus defined the nature of the numerical problem that we must solve, let us next look at possible solutions. It might appear that the most straightforward approach would be to evaluate $\langle A \rangle$ in equation (38) by numerical quadrature, for instance using Simpson's rule. It is easy to see, however, that such a method is completely useless even if the number of independent coordinates $DN$ ($D$ is the dimensionality of the system) is still very small $\mathcal{O}(100)$. Suppose that we plan to carry out the quadrature by evaluating the integrand on a mesh of points in the $DN$-dimensional configuration space. Let us assume that we take $m$ equidistant points along each coordinate axis. The total number of points at which the integrand must be evaluated is then equal to $m^{DN}$. For all but the smallest systems this number becomes astronomically large, even for small values of $m$. For instance, if we take 100 particles in three dimensions, and $m = 5$, then we would have to evaluate the integrand at $10^{210}$ points! Computations of such magnitude cannot be performed in the known universe. And this is fortunate, because the answer that would be obtained would have been subject to a large statistical error. After all, numerical quadratures work best on functions that are smooth over distances corresponding to the mesh size. But for most intermolecular potentials, the Boltzmann-factor in equation (38) is a rapidly varying function of the particle coordinates. Hence an accurate quadrature requires a small mesh spacing (*i.e.*, a large value of $m$). Moreover, when evaluating the integrand for a dense liquid (say), we would find that for the overwhelming majority of points this Boltzmann factor is vanishingly small. For instance, for a fluid of 100 hard spheres at the freezing point, the Boltzmann factor would be non-zero for 1 out of every $10^{260}$ configurations!

The above example clearly demonstrates that better numerical techniques are needed to compute thermal averages. One such a technique is the Monte Carlo method or, more precisely, the Monte Carlo importance-sampling scheme introduced 1953 by Metropolis, Rosenbluth, Rosenbluth, Teller and Teller [10]. The application of this method to the numerical simulation of dense molecular systems is the subject of the present chapter.

## 5.1 Importance Sampling

Before discussing importance sampling, let us first look at the simplest Monte Carlo technique, *i.e.*, random sampling. Suppose we wish to evaluate numerically a one dimensional integral $I$ :

$$I = \int_a^b \mathrm{d}x \; f(x) \, . \tag{39}$$

Instead of using a conventional quadrature where the integrand is evaluated at predetermined values of the abscissa, we could do something else. Note that equation (39) can be rewritten as:

$$I = (b - a) \, \langle f(x) \rangle \;\; , \tag{40}$$

where $\langle f(x) \rangle$ denotes the unweighted average of $f(x)$ over the interval $[a, b]$. In brute force Monte Carlo, this average is determined by evaluating $f(x)$ at a large number (say, $L$) of $x$-values randomly distributed over the interval $[a, b]$. It is clear that as $L \to \infty$, this procedure should yield the correct value for $I$. However, as with the conventional quadrature procedure, this method is of little use to evaluate averages such as in equation (38) because most of the computing is spent on points where the Boltzmann factor is negligible. Clearly it would be much preferable to sample many points in the region where the Boltzmann factor is large, and few elsewhere. This is the basic idea behind importance sampling.

How should we distribute our sampling through configuration space? To see this, let us first consider a simple, one-dimensional example. Suppose we wish to compute the definite integral in equation (39) by Monte Carlo sampling, but with the sampling points distributed non-uniformly over the interval $[a, b]$ (for convenience we assume $a = 0$ and $b = 1$), according to some non-negative probability-density $w(x)$. Clearly, we can rewrite equation (39) as:

$$I = \int_0^1 \mathrm{d}x \; w(x) \frac{f(x)}{w(x)} \, . \tag{41}$$

Let us assume that we know that $w(x)$ is the derivative of another (non-negative, non-decreasing) function $u(x)$, with $u(0) = 0$ and $u(1) = 1$ (these boundary conditions imply that $w(x)$ is normalized). Then $I$ can be written as :

$$I = \int_0^1 \mathrm{d}u \; \frac{f[x(u)]}{w[x(u)]}. \tag{42}$$

In equation (42) we have written $x(u)$ to indicate that if we consider $u$ as the integration variable, then $x$ must be expressed as a function of $u$. The next step is to generate $L$ random values of $u$ uniformly distributed in the interval $[0, 1]$. We then obtain the following estimate for $I$ :

$$I \approx \frac{1}{L} \sum_{i=1}^{L} \frac{f[x(u_i)]}{w[x(u_i)]} \, . \tag{43}$$

What have we gained by rewriting $I$ in this way? The answer depends crucially on our choice for $w(x)$. To see this, let us estimate $\sigma_I^2$, the variance in $I_L$, where $I_L$ denotes the estimate for $I$ obtained from equation (43) with $L$ random sample points:

$$\sigma_I^2 = \frac{1}{L^2} \sum_{i=1}^{L} \sum_{j=1}^{L} \left\langle \left( \frac{f[x(u_i)]}{w[x(u_i)]} - \langle f/w \rangle \right) \left( \frac{f[x(u_j)]}{w[x(u_j)]} - \langle f/w \rangle \right) \right\rangle \, , \tag{44}$$

where the angular brackets denote the true average, *i.e.*, the one that would be obtained in the limit $l \to \infty$. As different samples $i$ and $j$ are assumed to be totally independent, all cross terms in equation (44) vanish, and we are left with:

$$\begin{aligned} \sigma_I^2 &= \frac{1}{L^2} \sum_{i=1}^{L} \left\langle \left( \frac{f[x(u_i)]}{w[x(u_i)]} - \langle f/w \rangle \right)^2 \right\rangle \\ &= \frac{1}{L} \left[ \left\langle (f/w)^2 \right\rangle - \langle f/w \rangle^2 \right] \, . \end{aligned} \tag{45}$$

Equation (45) shows that the variance in $I$ still goes as $1/L$, but the magnitude of this variance can be reduced greatly by choosing $w(x)$ such that $f(x)/w(x)$ is a smooth function of $x$. Ideally we should have $f(x)/w(x)$ constant, in which case the variance would vanish altogether. In contrast, if $w(x)$ is constant, as is the case for the brute force Monte Carlo sampling, then the relative error in $I$ can become very large. For instance, if we are sampling in a (multi-dimensional) configuration space of volume $\Omega$, of which only a small fraction $f$ is accessible (for instance, $f = 10^{-260}$, see previous section), then the relative error that results in a brute-force MC sampling will be of order $1/(Lf)$. As the integrand in equation (38) is only non-zero for those configurations where the Boltzmann factor is non-zero, it would clearly be advisable to carry out a non-uniform Monte Carlo sampling of configuration space, such that the weight-function $w$ is approximately proportional to the Boltzmann factor. Unfortunately, the simple importance sampling scheme described above cannot be used to sample multidimensional integrals over configuration space, such as equation (38). The reason is simply that we do not know how to construct a transformation such as the one from equation (41) to equation (42) that would enable us to generate points in configuration-space with a probability-density proportional to the Boltzmann factor. In fact, a necessary (but not nearly sufficient) condition for the solution of the latter problem is that we must be able to compute analytically the partition function of the system under study. If we could do that for the systems that are of interest to us, there would hardly be any need for computer simulation.

## 5.2 The Metropolis Method

The closing lines of the previous section suggest that it is in general not possible to evaluate an integral, such as $\int \mathrm{d}\mathbf{r}^N \exp[-\beta\mathcal{U}(\mathbf{r}^N)]$ by direct Monte Carlo sampling. However, in many cases we are not interested in the configurational part of the partition function itself, but in averages of the type:

$$\langle A\rangle = \frac{\int \mathrm{d}\mathbf{r}^N \exp[-\beta\mathcal{U}(\mathbf{r}^N)]A(\mathbf{r}^N)}{\int \mathrm{d}\mathbf{r}^N \exp[-\beta\mathcal{U}(\mathbf{r}^N)]} \,. \tag{46}$$

Hence, we wish to know the *ratio* of two integrals. What Metropolis *et al.* [10] showed is that it is possible to devise an efficient Monte Carlo scheme to sample such a ratio[2]. In order to understand the Metropolis method, let us first look more closely at the structure of equation (46). In what follows we denote the configurational part of the partition function by $Z$:

$$Z \equiv \int \mathrm{d}\mathbf{r}^N \exp[-\beta\mathcal{U}(\mathbf{r}^N)] \,. \tag{47}$$

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[2] An interesting account of the early history of the Metropolis method may be found in: H.L. Anderson, J. Stat. Phys. **43** (1986) 731 and W.W. Wood, in: *Molecular Dynamics Simulations of Statistical Mechanical Systems*, eds. G. Ciccotti and W.G. Hoover, (North-Holland, Amsterdam, 1986) pg. 3.

Note that the ratio $\exp(-\beta\mathcal{U})/Z$ in equation (46) is the probability density to find the system in a configuration around $\mathbf{r}^N$. Let us denote this probability density by

$$\mathcal{N}(\mathbf{r}^N) \equiv \frac{\exp[-\beta\mathcal{U}(\mathbf{r}^N)]}{Z}.$$

Clearly, $\mathcal{N}(\mathbf{r}^N)$ is non-negative.

Suppose now that we are somehow able to randomly generate points in configuration-space according to this probability distribution $\mathcal{N}(\mathbf{r}^N)$. This means that, on average, the number of points $n_i$ generated per unit volume around a point $\mathbf{r}^N$ is equal to $L\mathcal{N}(\mathbf{r}^N)$, where $L$ is the total number of points that we have generated. In other words:

$$\langle A\rangle \approx \frac{1}{L}\sum_{i=1}^{L} n_i\, A(\mathbf{r}_i^N)\ . \tag{48}$$

By now the reader is almost certainly confused about the difference, if any, between equation (48) and equation (43) of section 5.1. The difference is that in the case of equation (43) we know *a priori* the probability of sampling a point in a (hyper)volume $d\mathbf{r}^N$ around $\mathbf{r}^N$. In other words we know both $\exp[-\beta\mathcal{U}(\mathbf{r}^N)]$ *and* $Z$. In contrast, in equation (48) we know only $\exp[-\beta\mathcal{U}(\mathbf{r}^N)]$, *i.e.*, we know only the relative, but not the absolute probability of visiting different points in configuration space.

Let us next consider how to generate points in configuration space with a relative probability proportional to the Boltzmann factor. The general approach is first to prepare the system under study in a configuration $\mathbf{r}^N$, which we denote by $o$ (old), that has a non-vanishing Boltzmann factor $\exp[-\beta\mathcal{U}(o)]$. This configuration may, for example, correspond to a regular crystalline lattice with no hard-core overlaps. Next, we generate a new trial configuration $\mathbf{r}'^N$, which we denote by $n$ (new), by adding a small random displacement $\Delta$ to $o$. The Boltzmann factor of this trial configuration is $\exp[-\beta\mathcal{U}(n)]$. We must now decide whether we will accept or reject the trial configuration. There are many possible rules for making this decision, that satisfy the constraint that on average the probability of finding the system in a configuration $n$ is proportional to $\mathcal{N}(n)$. Here we discuss only the Metropolis scheme, because it is simple and generally applicable.

Let us now 'derive' the Metropolis scheme to determine the transition probability $\pi(o \to n)$ to go from configuration $o$ to $n$. It is convenient to start with a thought experiment (actually a thought simulation). We carry out a very large number (say $M$) Monte Carlo simulations in parallel, where $M$ is much larger than the total number of accessible configurations. We denote the number of points in any configuration $o$ by $m(o)$. We wish that, on average, $m(o)$ is proportional to $\mathcal{N}(o)$. There is one obvious condition that the matrix elements $\pi(o \to n)$ must satisfy: namely that they do not destroy such an equilibrium distribution once it is reached. This means that, in equilibrium, the average number of accepted trial moves that result in the system leaving state $o$ must be exactly equal to the number of accepted trial moves from all other states $n$ to state $o$. It is convenient to impose a much stronger condition, namely that in equilibrium the average number of accepted moves from $o$ to any other state $n$ is exactly canceled by the number of reverse moves. This detailed balance condition implies the following:

$$\mathcal{N}(o)\pi(o \rightarrow n) = \mathcal{N}(n)\pi(n \rightarrow o) \; . \tag{49}$$

There are many possible forms of the transition matrix $\pi(o \rightarrow n)$ that satisfy equation (49). Let us look how $\pi(o \rightarrow n)$ is constructed in practice. We recall that a Monte Carlo move consists of two stages: first we perform a trial move from state $o$ to state $n$. We denote the transition matrix that determines the probability to perform a trial move from $i$ to $j$ by $\alpha(o \rightarrow n)$. $\alpha$ is usually referred to as the underlying matrix of Markov chain [11]. The next stage is the decision to either accept or reject this trial move. Let us denote the probability of accepting a trial move from $o$ to $n$ by $\mathrm{acc}(o \rightarrow n)$, Clearly

$$\pi(o \rightarrow n) = \alpha(o \rightarrow n) \times \mathrm{acc}(o \rightarrow n) \, . \tag{50}$$

In the original Metropolis scheme, $\alpha$ is chosen to be a symmetric matrix. However, in later sections we shall see several examples where $\alpha$ is *not* symmetric. If $\alpha$ is symmetric, we can rewrite equation (49) in terms of the $\mathrm{acc}(o \rightarrow n)$ :

$$\mathcal{N}(o) \times \mathrm{acc}(o \rightarrow n) = \mathcal{N}(n) \times \mathrm{acc}(n \rightarrow o) \; . \tag{51}$$

From equation (51) follows:

$$\frac{\mathrm{acc}(o \rightarrow n)}{\mathrm{acc}(n \rightarrow o)} = \frac{\mathcal{N}(n)}{\mathcal{N}(o)} = \exp\{-\beta[\mathcal{U}(n) - \mathcal{U}(o)]\} \; . \tag{52}$$

Again, there are many possible choices for $\mathrm{acc}(o \rightarrow n)$ that satisfy this condition (and the obvious condition that the probability $\mathrm{acc}(o \rightarrow n)$ cannot exceed 1). The choice of Metropolis *et al.* is:

$$\begin{array}{rcll} \mathrm{acc}(o \rightarrow n) & = & \mathcal{N}(o)/\mathcal{N}(n) & \text{if } \mathcal{N}(n) < \mathcal{N}(o) \\ & = & 1 & \text{if } \mathcal{N}(n) \geq \mathcal{N}(o) \; . \end{array} \tag{53}$$

Other choices for $\mathrm{acc}(o \rightarrow n)$ are possible (for a discussion, see for instance [12]), but the original choice of Metropolis *et al.* appears to result in a more efficient sampling of configuration space than most other strategies that have been proposed.

In summary, then, in the Metropolis scheme, the transition probability for going from state $o$ to state $n$ is given by:

$$\begin{array}{rcll} \pi(o \rightarrow n) & = & \alpha(o \rightarrow n) & \mathcal{N}(n) \geq \mathcal{N}(o) \\ & = & \alpha(o \rightarrow n)[\mathcal{N}(n)/\mathcal{N}(o)] & \mathcal{N}(n) < \mathcal{N}(o) \\ \pi(o \rightarrow o) & = & 1 - \sum_{n \neq o} \pi(o \rightarrow n) & . \end{array} \tag{54}$$

Note that we still have not specified the matrix $\alpha$, but for the fact that it must be symmetric. This reflects the fact that there is a considerable freedom in the choice of our trial moves. We will come back to this point in subsequent sections.

One thing that we have not yet explained is how to decide whether a trial move is to be accepted or rejected. The usual procedure is as follows. Suppose that we have generated a trial move from state $o$ to state $n$, with $\mathcal{U}(n) > \mathcal{U}(o)$. According to equation (52) this trial move should be accepted with a probability:

$$\mathrm{acc}(o \rightarrow n) = \exp\{-\beta[\mathcal{U}(n) - \mathcal{U}(o)]\} < 1\,.$$

In order to decide whether to accept or reject the trial move, we generate a random number, denoted by Ranf, from a uniform distribution in the interval $[0, 1]$. Clearly, the probability that Ranf is less than $\mathrm{acc}(o \rightarrow n)$ is equal to $\mathrm{acc}(o \rightarrow n)$. We now accept the trial move if Ranf $< \mathrm{acc}(o \rightarrow n)$, and reject it otherwise. This rule guarantees that the probability to accept a trial move from $o$ to $n$ is indeed equal to $\mathrm{acc}(o \rightarrow n)$. Obviously it is very important that our random number generator does indeed generate numbers uniformly in the interval $[0, 1]$. Otherwise the Monte Carlo sampling will be biased. The quality of random number generators should never be taken for granted. A good discussion of random number generators can be found in the book Numerical recipes [13] and in the book on Monte Carlo techniques by Kalos and Whitlock [14].

Thus far, we have not mentioned another condition that $\pi(o \rightarrow n)$ should satisfy, namely that it is *ergodic*, *i.e.*, that every accessible point in configuration space can be reached in a finite number of Monte Carlo steps from any other point. Although there are simple MC schemes that are guaranteed to be ergodic, these are often not the most efficient schemes. Conversely, there are many efficient Monte Carlo schemes that have either not been proven to be ergodic or, worse, been proven to be non-ergodic. The solution is usually to mix the efficient, non-ergodic scheme with an occasional trial move of the less-efficient but ergodic scheme. The method as a whole will then be ergodic (at least, in principle).

# 6 A basic Monte Carlo algorithm

It is difficult to talk about Monte Carlo or Molecular Dynamics programs in abstract terms. The best way to explain how such programs work is to write them down. This will be done in the present section.

Most Monte Carlo or Molecular Dynamics programs are only a few hundred to several thousand lines long. This is very short compared to, for instance, a typical quantum-chemistry code. For this reason, it is not uncommon that a simulator will write many different programs that are tailor-made for specific applications. The result is that there is no such thing as a standard Monte Carlo or Molecular Dynamics program. However, the cores of most MD/MC programs are, if not identical, at least very similar. Below, we briefly describe such a core program.

## 6.1 The algorithm

The prime purpose of the kind of Monte Carlo or Molecular Dynamics program that we shall be discussing is to compute equilibrium properties of classical many-body systems. From now on, we shall refer to such programs simply as MC or MD programs, although it should be remembered that there exist many other applications of the Monte Carlo method (and, to a lesser extent, of the Molecular Dynamics method). Let us now look at a simple Monte Carlo program.

In the previous section the Metropolis method is introduced as a Markov process in which a random walk is constructed in such a way that the probability to visit a particular point $\mathbf{r}^N$ is proportional to the Boltzmann factor $\exp[-\beta\mathcal{U}(\mathbf{r}^N)]$. There are many ways to construct such a random walk. In the approach introduced by Metropolis *et al.* [10] the following scheme is proposed:

1. select a particle at random, and calculate its energy $\mathcal{U}(\mathbf{r}^N)$,
2. give the particle a random displacement:$r' = r + \Delta$, and calculate its new energy $\mathcal{U}(\mathbf{r'}^N)$,
3. accept the move from $\mathbf{r}^N$ to $\mathbf{r'}^N$ with probability

$$\text{acc}(o \to n) = \min\left(1, \exp\{-\beta[\mathcal{U}(\mathbf{r'}^N) - \mathcal{U}(\mathbf{r}^N)]\}\right) . \tag{55}$$

## 6.2 Technical details

In this section, we discuss a number of computational tricks that are of great practical importance for the design of an efficient simulation program. It should be stressed that most of these tricks, although undoubtedly very useful, are not unique and have no deep physical significance. But that does not imply that the use of such computational tools is free of risks or subtleties. Ideally, schemes to save computer time should not affect the results of a simulation in a systematic way. Yet, in some cases, the time-saving tricks that are used do have a measurable effect on the outcome of a simulation. This is particularly true for the different procedures that are used to avoid explicit calculation of intermolecular interactions between particles that are far apart. Fortunately, once this is recognized, it is usually possible to estimate the undesirable side-effect of our time-saving scheme and to correct for it.

### 6.2.1 Boundary conditions

Monte Carlo and Molecular Dynamics simulations of atomic or molecular systems aim to provide information about the properties of a macroscopic sample. Yet, the number of degrees of freedom that can be conveniently handled in present-day computers ranges from a few hundred to a few million. Most simulations probe the structural and thermodynamical properties of a system of a few hundred to a few thousand particles. Clearly this number is still far removed from the thermodynamic limit. To be more precise, for such small systems it cannot be safely assumed that the choice of the boundary conditions (*e.g.*, free or hard or periodic) has a negligible effect on the properties of the system. In fact, in a three-dimensional $N$-particle system with free boundaries, the fraction of all molecules that is at the surface is proportional to $N^{-1/3}$. For instance, in a simple cubic crystal of 1000 atoms, some 49% of all atoms are at the surface, and for $10^6$ atoms this fraction has only decreased to 6%.

In order to simulate bulk phases it is essential to choose boundary conditions that mimic the presence of an infinite bulk surrounding our $N$-particle model system. This is usually achieved by employing periodic boundary conditions. The volume containing the $N$ particles is treated as the primitive cell of an infinite periodic lattice of identical cells (see figure 1). A given particle ($i$, say) now interacts with all other particles in this infinite periodic system, *i.e.*, all other particles in the same periodic cell and all particles (including its own periodic image) in all other cells. For instance, if we assume that all intermolecular interactions are pairwise additive, then the total potential energy of the $N$ particles in any one periodic box is

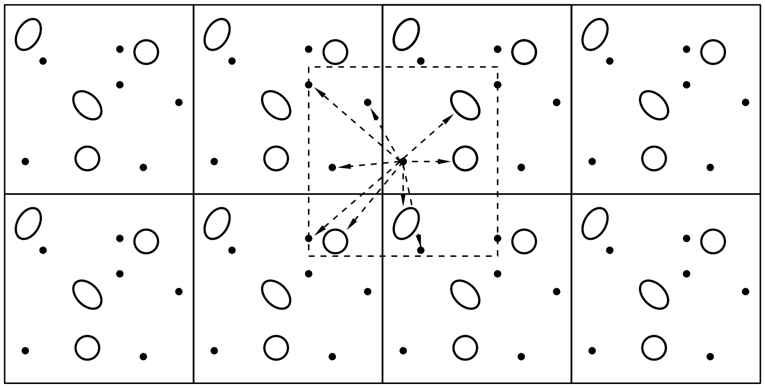

Figure 1: Schematic representation of periodic boundary conditions.

$$\mathcal{U}_{\rm tot} = \frac{1}{2} \sum_{i,j,\mathbf{n}}{}' u(|\mathbf{r}_{ij} + \mathbf{n}L|)$$

where $L$ is the diameter of the periodic box (assumed cubic, for convenience) and $\mathbf{n}$ is an arbitrary vector of three integer numbers, while the prime over the sum indicates that the term with $i = j$ is to be excluded when $\mathbf{n} = \mathbf{0}$. In this very general form, periodic boundary conditions are not particularly useful, because in order to simulate bulk behavior, we had to rewrite the potential energy as an infinite sum rather than a finite one[3]. In practice, however, we are often dealing

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[3] In fact, in the first MC simulation of three-dimensional Lennard-Jones particles, Wood and Parker [15] discuss the use of such infinite sums in relation to the now conventional approach discussed below.

with short-range interactions. In that case it is usually permissible to truncate all intermolecular interactions beyond a certain cut-off distance $r_c$. How this is done in practice is discussed below.

Although the use of periodic boundary conditions proves to be a surprisingly effective method to simulate homogeneous bulk systems, one should always be aware that the use of such boundary conditions may lead to spurious correlations that are not present in a truly macroscopic bulk system. In particular, one consequence of the periodicity of the model system is that only those fluctuations are allowed that have a wavelength that is compatible with the periodic lattice: the longest wavelength that still fits in the periodic box is the one for which $\lambda = L$. If long wavelength fluctuations are expected to be important (as, for instance, in the vicinity of a continuous phase transition), then one should expect problems with the use of periodic boundary conditions. Another unphysical effect that is a manifestation of the use of periodic boundary conditions, is the fact that the radial distribution function $g(r)$ of a dense atomic fluid is found to be not exactly isotropic [16].

Finally, it is useful to point out one common misconception about periodic boundary conditions: namely the idea that the boundary of the periodic box itself has any special significance. It has not. The origin of the periodic lattice of primitive cells may be chosen anywhere, and this choice will not affect any property of the model system under study. In contrast, what *is* fixed is the shape of the periodic cell, and its orientation.

### 6.2.2 Truncation of interactions

Let us now consider the case that we perform a simulation of a system with short-ranged interactions. In this context, short-ranged means that the total potential energy of a given particle $i$ is dominated by interactions with neighboring particles that are closer than some cut-off distance $r_c$. The error that results when we ignore interactions with particles at larger distances can be made arbitrarily small by choosing $r_c$ sufficiently large. If we use periodic boundary conditions, the case that $r_c$ is less than $L/2$ (half the diameter of the periodic box) is of special interest because in that case we need only consider the interaction of a given particle $i$ with the nearest periodic image of any other particles $j$ (see the dotted box in figure 1). If the intermolecular potential is not rigorously zero for $r \geq r_c$, truncation of the intermolecular interactions at $r_c$ will result in a systematic error in $\mathcal{U}^{\text{tot}}$. If the intermolecular interactions decay rapidly, one may correct for the systematic error by adding a tail-contribution to $\mathcal{U}^{\text{tot}}$:

$$\mathcal{U}^{\text{tot}} = \sum_{i<j} u_c(r_{ij}) + \frac{N\rho}{2} \int_{r_c}^{\infty} \mathrm{d}r \; u(r) 4\pi r^2 \tag{56}$$

where $u_c$ stands for the truncated potential energy function and $\rho$ is the average number density. In writing down this expression, it is implicitly assumed that the radial distribution function $g(r) = 1$ for $r > r_c$. Clearly, the nearest periodic image convention can only be applied if the tail correction is small. From equation (56) it can be seen that the t ail-correction to the potential energy is infinite unless the potential energy function $u(r)$ decays more rapidly than $r^{-3}$ (in three dimensions). This condition is satisfied if the long-range interaction between molecules is dominated by dispersion forces. However, for the very important case of Coulomb and dipolar interactions, the tail correction diverges and hence the nearest-image convention cannot be used for such systems. In such cases, the interactions with all periodic images should be taken into account explicitly.

There are several factors that make truncation of the potential a tricky business. First of all, it should be realized that although the absolute value of the potential energy function decreases with inter-particle separation $r$, for sufficiently large $r$, the number of neighbors is a rapidly increasing function of $r$. In fact, the number of particles at a distance $r$ of a given atom increases asymptotically as $r^{d-1}$, where $d$ is the dimensionality of the system. As an example, let us compute the effect of truncating the pair potential for simple example —the three-dimensional Lennard-Jones fluid. The pair potential for this rather popular model system is given by

$$u^{\mathrm{lj}}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{57}$$

The average potential energy (in three dimensions) of any given atom $i$ is given by

$$u_i = (1/2)\int_0^\infty \mathrm{d}r\, 4\pi r^2 \rho(r) u(r)$$

where $\rho(r)$ denotes the average number density at a distance $r$ from a given atom $i$. The factor (1/2) has been included to correct for double counting of intermolecular interactions. If we truncate the potential at a distance $r_c$, we ignore the tail contribution $u^{\mathrm{tail}}$

$$u^{\mathrm{tail}} \equiv (1/2)\int_{r_c}^\infty \mathrm{d}r\, 4\pi r^2 \rho(r) u(r) \tag{58}$$

where we have dropped the subscript $i$, because all atoms in the system are identical. To simplify the calculation of $u^{\mathrm{tail}}$, we assume that for $r \geq r_c$, the density $\rho(r)$ is equal to the average number density $\rho$. If $u(r)$ is the Lennard-Jones potential, we find for $u^{\mathrm{tail}}$,

$$\begin{aligned} u^{\mathrm{tail}} &= \frac{1}{2}4\pi\rho\int_{r_c}^\infty \mathrm{d}r\, r^2 u(r) \\ &= \frac{1}{2}16\pi\rho\epsilon\int_{r_c}^\infty \mathrm{d}r\, r^2\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \\ &= \frac{8}{3}\pi\rho\epsilon\sigma^3\left[\frac{1}{3}\left(\frac{\sigma}{r_c}\right)^{9} - \left(\frac{\sigma}{r_c}\right)^{6}\right]. \end{aligned} \tag{59}$$

For a cutoff distance $r_c = 2.5\ \sigma$ the potential has decayed to a value that is about $1/60^{\text{th}}$ of the well depth. This seems to be a very small value, but in fact the tail correction is usually non-negligible. For instance, at a density $\rho\sigma^3 = 1$, we find $u^{\text{tail}} = -0.535\epsilon$. This number is certainly not negligible compared to the total potential energy per atom (almost 10% at a typical liquid density), hence although we can truncate the potential at 2.5 $\sigma$, we cannot ignore the effect of this truncation.

### 6.2.3 Initialization

In order to start the simulation, we should assign initial positions to all particles in the system. As the equilibrium properties of the system do not (or, at least, should not) depend on the choice of initial conditions, all reasonable initial conditions are in principle acceptable. If we wish to simulate the solid state of a particular model system, it is logical to prepare the system in the crystal structure of interest. In contrast, if we are interested in the fluid phase, we simply prepare the system in any convenient crystal structure. This crystal subsequently melts, because at the temperature and density of a typical liquid-state point, the solid state is not thermodynamically stable. Actually, one should be careful here, because the crystal structure may be meta-stable, even if it is not absolutely stable. For this reason, it is unwise to use a crystal structure as the starting configuration of a liquid close to the freezing curve. In such cases, it is better to use the final (liquid) configuration of a system at a higher temperature or lower density, where the solid is unstable and has melted spontaneously. In any event, it is usually preferable to use the final (well equilibrated) configuration of an earlier simulation at a nearby state point as the starting configuration for a new run and adjust the temperature and density to the desired values.

The equilibrium properties of a system should not depend on the initial conditions. If such a dependence is nevertheless observed in a simulation, there are two possibilities. The first is that our results reflect the fact that the system that we simulate really behaves non-ergodically. This is for instance the case in glassy materials or low-temperature, substitutionally disordered alloys. The second (and much more likely) explanation is that the system that we simulate is ergodic but that our sampling of configuration space is inadequate: in other words, we have not yet reached equilibrium!

### 6.2.4 Reduced units

In simulations it is often convenient to express quantities such as temperature, density, pressure etc. in reduced units. This means that we choose a convenient unit of energy, length and mass and then express all other quantities in terms of these basic units. In the example of a Lennard-Jones system, we consider we use a pair potential that is of the form u(r)=$\epsilon f(r/\sigma)$, (see equation (57)). A natural (though not unique) choice for our basic units is the following:

- unit of length: $\sigma$
- unit of energy: $\epsilon$
- unit of mass: $m$ (the mass of the atoms in the system)

from these basic units, all other units follow. For instance, our unit of time is

$$\sigma\sqrt{m/\epsilon}$$

and the unit of temperature is

$$\epsilon/k_B$$

In terms of these reduced units, denoted with superscript '*', the reduced pair potential $u^* \equiv u/\epsilon$ is a dimensionless function of the reduced distance $r^* \equiv r/\sigma$. For instance, the reduced form for the Lennard-Jones potential is

$$u^{*\mathrm{lj}}(r^*) = 4\left[\left(\frac{1}{r^*}\right)^{12} - \left(\frac{1}{r^*}\right)^{6}\right]. \tag{60}$$

With these conventions we can define the following reduced units: the potential energy $U^* = U\epsilon^{-1}$, the pressure $P^* = P\sigma^3\epsilon^{-1}$, the density $\rho^* = \rho\sigma^3$, and the temperature $T^* = k_B T\epsilon^{-1}$.

One may wonder why it is convenient to introduce reduced units. The most important reason is that there are (infinitely) many combinations of $\rho, T, \epsilon$ and $\sigma$ that all correspond to the same state in reduced units. This is, in fact, the law of corresponding states: the same simulation of a Lennard-Jones model can be used to study Ar at 60 K and a density of 840 kg/m$^3$ and Xe at 112 K and a density of 1617 kg/m$^3$. In reduced units, both simulations correspond to the state point $\rho^*$=0.5, $T^*$=0.5. If we had not used reduced units, we might have easily missed the equivalence of these two simulations. Another, practical, reason for using reduced units is the following: when we work with real (SI) units, we find that the absolute numerical values of the quantities that we are computing (*e.g.*, the average energy of a particle, or its acceleration) are either much less, or much larger, than 1. If we multiply several such quantities using standard floating-point multiplication, there is a distinct risk that, at some stage, we will obtain a result that creates an overflow or underflow. Conversely, in reduced units, almost all quantities of interest are of order 1 (say, between $10^{-3}$ and $10^3$). Hence, if we suddenly find a very large (or very small) number in our simulations (say $10^{42}$), then there is a good chance that we have made an error somewhere. In other words: reduced units make it easier to spot errors. Simulation results that are obtained in reduced units can always be translated back into real units. For instance, if we wish to compare the results of a simulation on a Lennard-Jones model at $T^* = 1$ and $P^* = 1$ with experimental data for Argon ($\epsilon/k_B$=119.8 K,

| quantity | reduced units | | real units |
|---|---|---|---|
| temperature | $T^* = 1$ | $\leftrightarrow$ | $T = 119.8$ K |
| density | $\rho^* = 0.7$ | $\leftrightarrow$ | $\rho = 1680$ kg/m$^3$ |
| time | $t^* = 0.005$ | $\leftrightarrow$ | $t = 2.1610^{-12}$ s |
| pressure | $P^* = 1$ | $\leftrightarrow$ | $P = 41.9$ MPa |

Table 1: Translation of reduced units to real units for Lennard-Jones Argon ($\epsilon/k_B$=119.8 K, $\sigma = 3.405\ 10^{-10}$m, M=0.03994 kg/mol).

$\sigma = 3.405\ 10^{-10}$m, M=0.03994 kg/mol), then we can use the translation given in Table 1 to covert our simulation parameters to real S.I units[4].

# 7 Trial moves

Now that we have specified the general structure of the Metropolis algorithm, we should consider its implementation. We shall not go into the problem of selecting intermolecular potentials for the model system under study. Rather, we shall simply assume that we have an atomic or molecular model system in a suitable starting configuration, and that we have specified all intermolecular interactions. We must now set up the underlying Markov chain, *i.e.*, the matrix $\alpha$. In more down to earth terms: we must decide how we are going to generate trial moves. We should distinguish between trial moves that involve only the molecular centers-of-mass and those that change the orientation or possibly even the conformation of a molecule.

## 7.1 Translational moves

We limit our discussion ot trial moves to those that translate the molecular center-of-mass. A perfectly acceptable method to create a trial displacement is to add random numbers between $-\Delta$ and $+\Delta$ to the $x$, $y$, and $z$ coordinates of the molecular center-of-mass:

$$\begin{aligned} x_i' &\to x_i + \Delta\,(\mathrm{Ranf} - 0.5) \\ y_i' &\to y_i + \Delta\,(\mathrm{Ranf} - 0.5) \\ z_i' &\to z_i + \Delta\,(\mathrm{Ranf} - 0.5)\ . \end{aligned} \tag{61}$$

where Ranf are random numbers uniformly distributed between 0 and 1. Clearly, the reverse trial move is equally probable (hence $\boldsymbol{\alpha}$ is symmetric)[5]. We are now

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[4] In what follows we will always use reduced units, unless explicitly indicated otherwise. We, therefore, omit the superscript '*' to denote reduced units.

[5] Although almost all published MC simulations on atomic and molecular systems generate trial displacements in a cube centered around the original center-of-mass position, this is by no

faced with two questions, namely: how large should we choose $\Delta$? And: should we attempt to move all particles simultaneously, or rather one at a time? In the latter case we should pick the molecule that is to be moved at random, to ensure that the underlying Markov chain remains symmetric. All other things being equal, we should choose the most efficient sampling procedure. But, to this end, we must first define what we mean by efficient sampling. In very vague terms, sampling is efficient if it gives you good value for money. Good value in a simulation corresponds to high statistical accuracy, and 'money' is simply *money*: the money that buys your computer time and even your own time. For the sake of the argument, we assume the average scientific programmer is poorly paid. In that case we only have to worry about your computer budget [6]. Then we could use the following definition of an optimal sampling scheme: A Monte Carlo sampling scheme can be considered optimal if it yields the lowest statistical error in the quantity to be computed for a given expenditure of computing budget. Usually, computing budget is equivalent to CPU time.

From this definition it is clear that, in principle, a sampling scheme may be optimal for one quantity but not for another. Actually, the above definition is all but useless in practice (as are most definitions). It is just not worth the effort to measure the error estimate in, for instance, the pressure, for a number of different Monte Carlo sampling schemes in a series of runs of fixed length. However, it is reasonable to assume that the mean-square error in the observables is inversely proportional to the number of uncorrelated configurations visited in a given amount of CPU time. And the number of independent configurations visited is a measure for the distance covered in configuration space. This suggests a more manageable, albeit rather ad hoc, criterion to estimate the efficiency of a Monte Carlo sampling scheme: namely the sum of the squares of all accepted trial displacements divided by computing time. This quantity should be distinguished from the mean-square displacement per unit of computing time, because the latter quantity goes to zero in the absence of diffusion (*e.g.*, in a solid or a glass), whereas the former does not.

Using this criterion it is easy to show that for simulations of condensed phases it is usually advisable to perform random displacements of one particle at a time (as we shall see later, the situation is different for correlated displacements). To see why random single-particle moves are preferred, consider a system of $N$ spherical particles, interacting through a potential energy function $\mathcal{U}(\mathbf{r}^N)$. Typically, we expect that a trial move will be rejected if the potential energy of the system

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means the only possibility. Sometimes it is more convenient to generate trial moves in a spherical volume, and it is not even necessary that the distribution of trial moves in such a volume is uniform, as long as it has inversion symmetry. For an example of a case where another sampling scheme is preferable, see: W.G.T. Kranendonk and D. Frenkel, Mol. Phys., **64** (1988) 403.

[6] Still, we should stress that it is not worthwhile to spend a lot of your time developing a fancy computational scheme that will only be marginally better than existing, simpler schemes, unless your program will run very often and speed is crucial.

changes by much more than $k_BT$. At the same time, we try to make the Monte Carlo trial steps as large as is possible without having a very low acceptance. A displacement that would, on average, give rise to an increase of the potential energy by $k_BT$ would still have a reasonable acceptance. In the case of a single-particle trial move we then have:

$$\begin{aligned} \langle \Delta \mathcal{U} \rangle &= \left\langle \frac{\partial \mathcal{U}}{\partial r_i^\alpha} \right\rangle \overline{\Delta r_i^\alpha} &+& \frac{1}{2} \left\langle \frac{\partial^2 \mathcal{U}}{\partial r_i^\alpha \partial r_i^\beta} \right\rangle \overline{\Delta r_i^\alpha \Delta r_i^\beta} &+& \cdots \\ &= 0 &+& f(\mathcal{U})\,\overline{\Delta r_i^2} &+& \mathcal{O}(\Delta^4) \end{aligned} \tag{62}$$

where the angular brackets denote averaging over the ensemble, and the horizontal bar denotes averaging over random trial moves. The second derivative of $\mathcal{U}$ has been absorbed into the function $f(\mathcal{U})$, the precise form of which does not concern us here. If we now equate $\langle \Delta \mathcal{U} \rangle$ on the right-hand side of equation (62) to $k_BT$, we find the following expression for $\overline{\Delta r_i^2}$:

$$\overline{\Delta r_i^2} \approx k_BT/f(\mathcal{U}) \tag{63}$$

If we attempt to move $N$ particles, one at a time, most of the computation involved is spent on the evaluation of the change in potential energy. Assuming that we use a neighbor list or a similar time-saving device, the total time spent on evaluation the potential energy change is proportional to $nN$, where $n$ is the average number of interaction partners per molecule. The sum of the mean-square displacements will be proportional to $N\overline{\Delta r^2} \sim Nk_BT/f(\mathcal{U})$. And hence the mean-square displacement per unit of CPU-time will be proportional to: $k_BT/(n\,f(\mathcal{U}))$. Now suppose that we try to move all particles at once. The cost in CPU time will still be proportional to $nN$. But, using the same reasoning as in equations (62) and (63), we estimate that the sum of the mean-square displacements is smaller by a factor $1/N$. Hence the total efficiency will be down by this same factor. This simple argument explains why most simulators use single-particle, rather than collective trial moves. It is important to note that we have assumed that a collective MC trial move consists of $N$ independent trial displacements of the particles. However, efficient collective MC moves *can* be constructed if the trial displacements of the individual particles are not chosen independently.

Next, consider the choice of the parameter $\Delta$ which determines the size of the trial move. How large should $\Delta$ be? If it is very large, it is likely that the resulting configuration will have a high energy and the trial move will probably be rejected. If it is very small, the change in potential energy is probably small and most moves will be accepted. In the literature, one often finds the mysterious statement that an acceptance of approximately 50% should be optimal. This statement is not necessarily true. The optimum acceptance ratio is the one that leads to the most efficient sampling of configuration space. If we express efficiency as mean-square displacement per CPU-time, it is easy to see that different Monte Carlo codes will have different optimal acceptance ratio's. The reason is that it makes a crucial difference if the amount of computing required to test whether a trial move is accepted depends on the magnitude of the move.

In the conventional Metropolis scheme, all continuous interactions have to be computed before a move can be accepted of rejected. Hence, for continuous potentials, the amount of computation does not depend on the size of a trial move. In contrast, for simulations of molecules with hard repulsive cores, a move can be rejected as soon as overlap with any neighbor is detected. In that case, a rejected move is cheaper than an accepted one, and hence the average computing time per trial move goes down as the step-size is increased. As a result, the optimal acceptance ratio for hard-core systems is appreciably lower than for systems with continuous interactions. Exactly how much depends on the nature of the program, in particular on whether it is a scalar or a vector code (in the latter case hard-core systems are treated much like continuous systems), how the information about neighbor-lists is stored, and even on the computational 'cost' of random numbers and exponentiation. The consensus seems to be that for hard-core systems the optimum acceptance ratio is closer to 20% than to 50%.

## 7.2 Composite moves

It is easiest to start our discussion of composite moves by considering a practical example, namely Monte Carlo sampling of polymers. Polymers are typically modeled as a string of monomers connected together by a fixed spacing. One approach to simulating polymers is called reptation. In this approach a trial move consists of removing a monomer at one end of the polymer and adding a monomer at a random orientation at the other end. However, we would like to move the entire polymer to a new shape in one trial move. An arbitrary attempt to do this move or to add a polymer to the system will almost always be rejected. To overcome this low acceptance rate, we need to use a smarter Monte Carlo scheme. We shall use trial moves that are no longer completely random; the moves are biased in such a way that the trial position and shape of the polymer to be moved has an enhanced probability to fit into the existing configuration. A similar approach also will be used for polymer insertion and removal. Biasing a Monte Carlo trial move, means that the probability to generate forward and reverse trial moves are no longer equal, that is, $\alpha(o \rightarrow n) \neq \alpha(n \rightarrow o)$. To satisfy detailed balance, we also must change the acceptance rule.

The starting point for the configurational bias Monte Carlo technique is the static Monte Carlo scheme introduced by Rosenbluth and Rosenbluth in 1955 to sample polymer conformations [1]. In a static Monte Carlo scheme, each new configuration is generated from scratch. The problem with the Rosenbluth scheme is that the probability of generating a polymer configuration is *not* proportional to its Boltzmann weight. To correct for this bias, we have to weight every generated configuration by the "Rosenbluth weight"(see below). In the configurational bias Monte Carlo method, we use the Rosenbluth scheme to generate trial moves, and we use the Rosenbluth weight to bias the *acceptance* of these trial moves. As we shall show, this procedure guarantees that all polymer conformations are generated with the correct Boltzmann weight. Note that the configurational bias Monte Carlo algorithm is a dynamic rather than a static method because new configurations are generated by applying a trial move to an existing configuration.

To illustrate the basic idea, we show how the configurational bias Monte Carlo algorithm works for a lattice model consisting of $N$ polymers each consisting of $\ell$ monomers. The algorithm consists of the following steps:

1. Choose a polymer at random, retrace its conformation , and determine its Rosenbluth weight $W(o)$. In the following we discuss how to determine $W(o)$.
2. Generate a trial conformation at a new position using the Rosenbluth scheme to grow the entire polymer and compute its Rosenbluth weight $W(n)$.
3. Accept the trial move with a probability

$$\mathrm{acc}(o \to n) = \min[1, W(n)/W(o)]. \tag{64}$$

In practice, step 2 is carried out before step 1. The reason is that the generation of a new trial configuration often is unsuccessful. In that case, the trial move can be rejected right away, and there is no need to compute the Rosenbluth weight of the old configuration.

To determine the Rosenbluth weight of the old configuration denoted by $o$, we use the following steps

1. Measure the energy of interaction $u_1(o)$ of the first monomer with other polymers and compute $w_1(o) = k\exp[-\beta u_1(o)]$.
2. To compute the Rosenbluth weight for the remainder of the chain, we determine the interaction energy $u_i(j)$ of monomer $i$ at its actual position, and the energy it would have had if it had been placed in any of the other $k-1$ sites (labeled by $j$) neighboring the actual position of monomer $i-1$ . The energy $u_i(j)$ includes all interactions of monomer $i$ with other polymers in the system and with monomers 1 through $i-1$ of the same polymer. These energies are used to calculate the weights $w_i(o)$:

$$w_i(o) = e^{-\beta u_i(o)} + \sum_{j=2}^{k} e^{-\beta u_i(j)}. \tag{65}$$

3. Once the entire chain has been retraced, we determine its Rosenbluth weight:

$$W(o) = \prod_{i=1}^{\ell} w_i(o). \tag{66}$$

The Rosenbluth scheme to generate a new trial conformation (denoted by $n$) of a polymer proceeds as follows .

1. The first monomer is inserted at a random position. Its energy is denoted by $u_1(n)$, and we define $w_1(n) \equiv k \exp[-\beta u_1(n)]$, where $k$ is the coordination number of the lattice. For example, $k = 6$ for a simple cubic lattice.

2. For the next monomer, with index $i$, there are $k$ possible trial directions. The energy of trial direction $j$ is denoted by $u_i(j)$. From the $k$ possible directions, we select one, say $n$, with a probability

$$p_i(n) = \frac{e^{-\beta u_i(n)}}{w_i(n)}, \tag{67}$$

   where the partial Rosenbluth weight $w_i(n)$ is defined as

$$w_i(n) \equiv \sum_{j=1}^{k} e^{-\beta u_i(j)}. \tag{68}$$

   Eqn. 67 biases the growing of the polymers in such a way that conformations with the lowest energy are selected with the highest probability. It does not include the interactions with monomers $i+1$ to $\ell$. Hence, the total energy of the polymer chain is given by $\mathcal{U}(n) = \sum_{i=1}^{\ell} u_i(n)$.

3. Step 2 is repeated until the entire polymer chain is grown. The total Rosenbluth weight of configuration $n$ is given by:

$$W(n) = \prod_{i=1}^{\ell} w_i(n). \tag{69}$$

We need to demonstrate that the acceptance rule (64) removes the bias introduced by the use of the Rosenbluth scheme to generate trial conformations. The probability of generating a particular conformation $n$ follows from the repeated use of eqn. 67:

$$\alpha(o \to n) = \prod_{i=1}^{\ell} \frac{e^{-\beta u_i(n)}}{w_i(n)} = \frac{e^{-\beta \mathcal{U}(n)}}{W(n)}. \tag{70}$$

Similarly, for the reverse move,

$$\alpha(n \to o) = \frac{e^{-\beta \mathcal{U}(o)}}{W(o)}. \tag{71}$$

Using (70) and (71) in the requirement of detailed balance imposes the following condition on the acceptance criterion

$$\frac{\mathrm{acc}(o \to n)}{\mathrm{acc}(n \to o)} = \frac{W(n)}{W(o)}. \tag{72}$$

Clearly, the acceptance criterion given in eqn. 64 satisfies this condition.

Next we consider a configurational bias Monte Carlo method for off-lattice systems. If the orientation of a monomer relative to a neighboring monomer is described by a continuous variable, then there is an essential difference with the lattice model. In the latter case all the possible orientations can be considered explicitly, and the corresponding Rosenbluth weight can be calculated exactly. For the continuum case, we cannot sample all possible orientations, and it is impossible to determine the exact Rosenbluth weight because an infinite number of orientations are possible. Hence, the scheme for lattice models, in which the Rosenbluth weight for all orientations is calculated, cannot be used for a continuum model. A possible solution would be to use a large but finite number of trial directions. Surprisingly, this approximation is not necessary. It is possible to devise a *rigorous* algorithm using an arbitrary subset of all possible trial directions. As a consequence, an off-lattice trial move looks very much like its lattice equivalent:

1. For the first monomer, a trial position $\mathbf{r}_n$ is selected at random, and the energy of this monomer is calculated. This energy is denoted by $u_1(n)$ and, as before, we define $w_1(n) = k \exp[-\beta u_1(n)]$.

2. For the subsequent monomers, $k$ trial bonds of length $b$ are generated, starting from the position of the previous monomer. We denote these trial bonds by $\{\mathbf{b}\}_k = (\mathbf{b}_1, \mathbf{b}_2, \cdots, \mathbf{b}_k)$. The end points of these vectors are distributed randomly on the surface of a sphere with radius $b$. For each trial position, the energy $u_i(\mathbf{b}_j)$ is calculated, and one of these positions is selected with probability
$$p_i(\mathbf{b}_n) = \frac{e^{-\beta u_i(\mathbf{b}_n)}}{w_i(n)}, \tag{73}$$
where
$$w_i(n) = \sum_{j=1}^{k} e^{-\beta u_i(\mathbf{b}_j)}. \tag{74}$$
In practice, it often is convenient to separate the intra-molecular (bending and torsion) potential energy from the non-bonded ("external") potential energy. In that case, the trial positions for the monomers are drawn from a Boltzmann distribution of "internal" energies, while the $u_i(\mathbf{b}_j)$ correspond to the external interactions.

3. Step 2 is repeated until the entire polymer of length $\ell$ has been grown, and the normalized Rosenbluth weight can be calculated:
$$\mathcal{W}(n) \equiv \frac{W(n)}{k^\ell} = \prod_{i=1}^{\ell} \frac{w_i(n)}{k}. \tag{75}$$

To compute the (off-lattice) Rosenbluth weight of the existing configuration of this polymer, we proceed as for the new configuration, except that we now generate $k-1$ randomly oriented trial monomers around every existing monomer. We compute the partial Rosenbluth weight, $w_i(o)$, for every set consisting of the actual monomer plus $k-1$ trial monomers. The total Rosenbluth weight of the existing chain conformation is $W(o) = \prod_{i=1} w_i(o)$, and the normalized weight is defined as $\mathcal{W}(o) \equiv W(o)/k^{\ell}$. Detailed balance is satisfied if we accept trial moves with a probability

$$P_{acc} = \mathrm{Min}(1, \mathcal{W}(n)/\mathcal{W}(o)).$$

# 8 Cluster moves

The crucial step in configurational bias Monte Carlo is that the 'bias' in the generation of trial conformations results in an enhanced acceptance of these trials moves. Ideally, we should like to bias the generation of trial moves in such a way that *every* move is always accepted. Surprisingly, it turns out that this is sometimes possible. Swendsen and Wang [2] (for a review, see ref. [3]) have shown that, at least for certain classes of lattice problems, it is possible to perform 'cluster moves' that have an acceptance probability of 100%.

The central idea behind the Swendsen-Wang (SW) scheme and subsequent extensions and modifications is to generate trial configurations with a probability that is proportional to the Boltzmann weight of that configuration. As a result, the subsequent trial moves can be accepted with 100% probability. I use a somewhat simplified derivation of the Swendsen-Wang for cluster moves based, again, on the condition for detailed balance. Consider and 'old' configuration (labeled by a superscript $o$) and a 'new' configuration, denoted by a superscript $n$. Detailed balance is satisfied if the following equality holds:

$$\begin{aligned} P_B^o P_{Gen}^o(\{cluster\}) P^{\{cl\}}(o \to n) P_{acc}(o \to n) \quad &= \\ P_B^n P_{Gen}^n(\{cluster\}) P^{\{cl\}}(n \to o) P_{acc}(n \to o) & \end{aligned} \tag{76}$$

where $P_B^{o(n)}$ is the Boltzmann weight of old (new) configuration, $P_{Gen}^o(\{cluster\})$ denotes the probability of generating a specific cluster, starting from the old configuration of the system. $P^{\{cl\}}(o \to n)$ is the probability to transform the generated cluster from the old to the new situation, and finally $P_{acc}(o \to n)$ is that acceptance probability of a given trial move. We can simplify eq. 76 in two ways: first of all, we impose that the *a priori* probability $P^{\{cl\}}(o \to n)$ is the same for the forward and reverse moves . Moreover, we wish to impose $P_{acc} = 1$ for both forward and reverse moves. This may not always be feasible. However, for the simple case that I discuss below, this is indeed possible. The detailed balance equation then becomes:

$$P_B^o P_{Gen}^o(\{cluster\}) = P_B^n P_{Gen}^n(\{cluster\}) \tag{77}$$

or

$$\frac{P^o_{Gen}(\{cluster\})}{P^n_{Gen}(\{cluster\})} = \frac{P^n_B}{P^o_B} = \exp(-\beta\Delta E) \ , \tag{78}$$

where $\Delta E$ is the difference in energy between the new and the old configurations. The trick is then to find a recipe for cluster generation that will satisfy eq.78. In order to illustrate how this works, consider the Ising model. The extension to many other models is straightforward.

**Ising model** For the construction of the Ising SW algorithm, the dimensionality of the model is irrelevant. Consider a given configuration of the spin system, with $N_p$ spin-pairs parallel and $N_a$ spin-pairs anti-parallel. The total energy of that configuration is:

$$E = (N_a - N_p)J$$

where $J$ denotes the strength of the nearest-neighbor interaction. The Boltzmann weight of that configuration is

$$P^o_B = \exp(-\beta J(N_a - N_p))/Z$$

where $Z$ is the partition function of the system. In general, $Z$ is unknown, but that is unimportant. We only use the fact that $Z$ is a constant. Next, we construct clusters by creating bonds between spin pairs according to the following recipe:

- If nearest neighbors are *anti-parallel*, they are not connected.
- If nearest neighbors are parallel, they are connect with probability $p$ and disconnected with probability $(1-p)$.

Here, I have assumed that $J$ is positive. If $J$ is negative (anti-ferromagnetic interaction), parallel spins are not connected, while anti-parallel spins are connected with a probability $p$.

In the case that we consider, there are $N_p$ parallel spin pairs. The probability that $n_c$ of these are connected and $n_b = N_p - n_c$ are 'broken' is:

$$P^o_{Gen}(\{cluster\}) = p^{n_c}(1-p)^{n_b} \ .$$

Note that this is the probability of connecting (*c.q.* break) a *specified* subset of all links between parallel spins. Once the connected bonds have been selected, we can define the clusters in the system. A cluster is a set of spins that are at least singly connected by bonds. We now choose our subset of clusters to flip. After the cluster flipping, the number of parallel and anti-parallel spin pairs will have changed, e.g.

$$N_p^{new} = N_p^{old} + \Delta$$

and (hence)

$$N_a^{new} = N_a^{old} - \Delta \ .$$

Therefore, the total energy of the system will have changed by an amount $-2J\Delta$:

$$E_{new} = E_{old} - 2J\Delta \ .$$

Let us now consider the probability to make the *reverse* move. In order to do this, we should generate the *same* cluster structure, but now starting from a situation where there are $N_p+\Delta$ parallel spin pairs and $N_a-\Delta$ anti-parallel pairs. As before, the bonds between anti-parallel pairs are assumed to be broken (this is compatible with the same cluster structure). We also know that the new number of connected bonds, $n'_c$ must be equal to $n_c$, *because the same number of connected bonds is required to generate the same cluster structure.* The difference appears when we consider how many of the bonds between parallel spins in the new configuration should be broken ($n'_b$). Using

$$N_p^{new} = n'_c + n'_b = n_c + n'_b = N_p^{old} + \Delta = n_c + n_b + \Delta$$

we see that

$$n'_b = n_b + \Delta$$

If we insert this in eq. 78, we obtain

$$\begin{aligned} \frac{P^o_{Gen}(\{cluster\})}{P^n_{Gen}(\{cluster\})} &= \\ \frac{p^{n_c}(1-p)^{n_b}}{p^{n_c}(1-p)^{n_b+\Delta}} &= \\ (1-p)^{-\Delta} &= \frac{P_B^n}{P_B^o} = \exp(2\beta J\Delta) \ . \end{aligned} \tag{79}$$

In order to satisfy this equation, we must have:

$$1 - p = \exp(-2\beta J)$$

or

$$p = 1 - \exp(-2\beta J) \ ,$$

which is the Swendsen-Wang rule.

## 8.1 General cluster moves

In general, it is not possible to design clusters such that trial moves are always accepted. However, it is often convenient to perform clustering to enhance the acceptance of trial moves. For instance, in molecular systems with very strong short-range attractions, trial moves that pull two neighboring particles apart are very likely to be rejected. It is therefore preferable to include trial moves that attempt to displace the tightly bound particles as a single cluster. In order to do this, we have to specify a rule to generate clusters. Let us assume that we have such a rule that tells us that particles $i$ and $j$ belong to a single cluster with probability $p(i,j)$ and are disconnected with a probability $1-p(i,j)$. $p(i,j)$ depends on the state ( relative distance, orientation, spin etc.) of particles $i$ and $j$, . Moreover, we impose that $p(i,j)$ is unchanged in a cluster move if both $i$ and $j$ belong to the cluster, and also if neither particle belongs to the cluster. For instance, $p(i,j)$ could depend on the current distance of $i$ and $j$ only. If we denote the potential energy of the old (new) configuration by $U_0$ ($U_1$), the detailed balance condition requires that

$$\exp(-\beta U_o)\prod_{kl}(1-p^f(k,l))P_{acc}(o\to n)=\exp(-\beta U_n)\prod_{kl}(1-p^r(k,l))P_{acc}(n\to o) \tag{80}$$

where $k$ denotes a particle *on* the cluster, and $l$ a particle outside it. The superscripts $f$ and $r$ denote forward and reverse moves. In writing Eqn. 80, we have used the fact that the probability to form bonds completely within, or completely outside, the cluster is the same for forward and reverse moves. From Eqn. 80, we derive an expression for the ratio of the acceptance probabilities:

$$R\equiv\frac{P_{acc}(0\to 1)}{P_{acc}(1\to 0)}=\exp(-\beta(U_1-U_0))\prod_{kl}\frac{(1-p^r(k,l))}{(1-p^f(k,l))}\ . \tag{81}$$

Clearly, many choices for $p_{kl}$ are possible. A particularly simple form was chosen by Wu, Chandler and Smit [4]) who assumed that $p(i,j)$ =1 for $r_{ij}$ less than a critical distance $r_c$ and $p(i,j)$=0 beyond that distance. Note that the acceptance rule in Eqn. 80 guarantees that two particles that did not belong to the same cluster in the old configuration will not end up at a distance less than $r_c$.

# 9 Other Ensembles

In the previous sections we have introduced Monte Carlo simulation as a technique to compute the average value of an arbitrary function $A(\mathbf{r}^N)$ of the coordinates of a system of N particles at constant temperature $T$ and volume $V$:

$$< A >_{NVT}=\frac{\int d\mathbf{r}^N\, A(\mathbf{r}^N)\exp(-\beta U(\mathbf{r}^N))}{\int d\mathbf{r}^N\,\exp(-\beta U(\mathbf{r}^N))}\ . \tag{82}$$

This average is usually referred to as the ‘canonical’ ensemble average. To be more precise, the true canonical ensemble average (eqn 38) includes the particle momenta. However, in all cases of practical interest, the integration over momenta can be carried out analytically, and therefore does not require numerical sampling.

Most Monte Carlo calculations to date have been performed in the constant-$NVT$ ensemble. However, it is sometimes advisable to perform a simulation where thermodynamic variables other than $N$,$V$ or $T$ are kept fixed. In the present section we discuss such simulations.

## 9.1 Isobaric-isothermal ensemble

The isobaric-isothermal (constant-$NPT$) ensemble is widely used in Monte Carlo simulations. This is not surprising because most real experiments are also carried out under conditions of controlled pressure and temperature. Moreover, constant-$NPT$ simulations can be used to measure the equation of state of a model system even if the virial expression for the pressure cannot be readily evaluated. This may, for instance, be the case for certain models of non-spherical hard-core molecules. But also for the increasingly important class of models where the (non-pairwise additive) potential energy function is computed *numerically* for each new configuration. Finally, it is often convenient to use constant-$NPT$ MC to simulate systems in the vicinity of a first-order phase transition, because at constant pressure the system is free (given enough time, of course) to transform completely into the state of lowest (Gibbs) free energy, whereas in a constant-$NVT$ simulation the system may be kept at a density where it would like to phase-separate into two bulk phases of different density, but is prevented from doing so by finite size effects.

Constant-pressure Monte Carlo simulations were first described by Wood [5] in the context of a simulation-study of two-dimensional hard disks. Although method introduced by Wood is very elegant, it is not readily applied to systems with arbitrary continuous potentials. McDonald [17] was the first to apply constant-$NPT$ simulations to a system with continuous intermolecular forces (a Lennard-Jones mixture), and it is the constant-pressure method of McDonald that is now being used almost universally, and that is discussed below.

I will derive the basic equations of constant-pressure Monte Carlo in a way that may appear unnecessarily complicated. However, this derivation has the advantage that the same framework can be used to introduce some of the other non-$NVT$ Monte Carlo methods to be discussed below. For the sake of convenience we shall initially assume that we are dealing with a system of $N$ identical atoms. The partition function for this system is given by:

$$Q(N,V,T) = \frac{1}{\Lambda^{3N}N!}\int_0^L \cdots \int_0^L d\mathbf{r}^N \exp(-\beta U(\mathbf{r}^N)) \; , \tag{83}$$

where $\Lambda = \sqrt{h^2/(2\pi mkT)}$ is the thermal de Broglie wavelength. It is convenient to rewrite eqn. 83 in a slightly different way. We have assumed that the system is contained in a cubic box with diameter $L = V^{\frac{1}{3}}$. We now define scaled coordinates $\mathbf{s}^N$, by:

$$\mathbf{r}_i = L\mathbf{s}_i$$

for $i = 1, 2, \cdots, N$. If we now insert these scaled coordinates in eqn 83 we obtain:

$$Q(N,V,T) = \frac{V^N}{\Lambda^{3N}N!}\int_0^1 \cdots \int_0^1 d\mathbf{s}^N \exp(-\beta U(\mathbf{s}^N; L)) \; . \tag{84}$$

In equation 84, we have written $U(\mathbf{s}^N;L)$ to indicate that $U$ depends on the *real* rather than the *scaled* distances between the particles. The expression for the Helmholtz free energy of the system is:

$$\begin{aligned} F(N,V,T) &= -kT\ln Q \\ &= -kT\ln(\frac{V^N}{\Lambda^{3N}N!}) - kT\ln(\int d\mathbf{s}^N \exp(-\beta U(\mathbf{s}^N;L))) \\ &= F_{id}(N,V,T) + F_{ex}(N,V,T)\ . \end{aligned} \tag{85}$$

In the last line of the above equation we have identified the two contributions to the Helmholtz free energy on the previous line as the ideal-gas expression plus an excess part. Let us now assume that the system is separated by a 'piston' from an ideal gas reservoir.

The total volume of the system plus reservoir is fixed at a value $V_0$. The total number of particles is $M$. Hence the volume accessible to the $m \equiv M - N$ ideal gas molecules is $V_0 - V$. The partition function of the total system is simply the product of the partition functions of the constituent sub-systems:

$$Q(N,m,V,V_0,T) = \frac{V^N(V_0-V)^m}{\Lambda^{3M}N!m!}\int d\mathbf{s}^m \int d\mathbf{s}^N \exp(-\beta U(\mathbf{s}^N;L))\ . \tag{86}$$

Note that the integral over the $\mathbf{s}^m$ scaled coordinates of the ideal gas yields simply 1. For the sake of compactness we have assumed that the thermal wavelength of the ideal gas molecules is also equal to $\Lambda$. The total free energy of this combined system is $F_{tot} = -kT\ln Q(N,m,V,V_0,T)$. Now let us assume that the 'piston' between the two subsystems is free to move, so that the volume $V$ of the $N$-particle subsystem can fluctuate. Of course, the most probable value of $V$ will be the one that minimizes the free energy of the combined system. The probability density $\mathcal{P}(V)$ that the $N$-particle subsystem has a volume $V$ is given by:

$$\mathcal{P}(V) = \frac{V^N(V_0-V)^m \int d\mathbf{s}^N \exp(-\beta U(\mathbf{s}^N;L))}{\int_0^{V_0} dV'\, V'^N(V_0-V')^m \int d\mathbf{s}^N \exp(-\beta U(\mathbf{s}^N;L'))} \tag{87}$$

We now consider the limit that the size of the reservoir tends to infinity ($V_0 \to \infty, M \to \infty, (m/V_0 \to \rho)$. In that limit, a small volume change of the small system does not change the pressure $P$ of the large system. In other words, the large system works as a manostat for the small system. In that case we can simplify eqns. 86 and 87. Note that in the limit $V/V_0 \to 0$ we can write:

$$(V_0 - V)^m = V_0^m(1-(V/V_0))^m \to V_0^m \exp(-mV/V_0).$$

Note that for $m \to \infty$, $\exp(-mV/V_0) \to \exp(-\rho V)$. But, as the reservoir contains an ideal gas, $\rho$ can be written as $\beta P$. With these substitutions, eqn. 87 becomes:

$$\mathcal{P}(V) = \frac{V^N \exp(-\beta PV) \int d\mathbf{s}^N \exp(-\beta U(\mathbf{s}^N;L))}{\int_0^{V_0} dV'\, V'^N \exp(-\beta PV') \int d\mathbf{s}^N \exp(-\beta U(\mathbf{s}^N;L'))}\ . \tag{88}$$

In the same limit, the difference in free energy between the combined system and the ideal-gas system in the absence of the $N$-particle subsystem is the well-known Gibbs free energy $G$ :

$$G(N,P,T) = -kT \ln \int dV \frac{V^N \exp(-\beta PV)}{\Lambda^{3N} N!} \int d\mathbf{s}^N \exp(-\beta U(\mathbf{s}^N; L)) \qquad (89)$$

Equation 88 is the starting point for constant-$NPT$ Monte Carlo simulations. The idea is that the probability-density to find the small system in a particular configuration of the $N$ atoms (as specified by $\mathbf{s}^N$) at a given volume $V$ is given by:

$$\mathcal{P}(V; \mathbf{s}^N) = \frac{V^N \exp(-\beta PV) \exp(-\beta U(\mathbf{s}^N; L))}{\int_0^{V_0} dV' \, V'^N \exp(-\beta PV') \int d\mathbf{s}^N \exp(-\beta U(\mathbf{s}^N; L'))} \, .$$

We can now carry out Metropolis sampling on the reduced coordinates $\mathbf{s}^N$ *and* the volume $V$, with a weight-function $\rho(\mathbf{s}^N, V)$ proportional to $\exp(-\beta\{U(\mathbf{s}^N, V) + PV - N\beta^{-1} \ln V\})$. In the constant-$N, P, T$ MC method, $V$ is simply treated as an additional coordinate, and trial moves in $V$ must satisfy the same rules as trial moves in $\mathbf{r}$ (in particular, we should maintain the symmetry of the underlying Markov chain). Let us assume that our trial moves consist of an attempted change of the volume from $V$ to $V' = V + \Delta V$, where $\Delta V$ is a random number uniformly distributed between over the interval $[-\Delta V_{max}, +\Delta V_{max}]$. In the Metropolis scheme such a random, volume changing move will be accepted if:

$$\exp(-\beta[U(\mathbf{s}^N, V') - U(\mathbf{s}^N, V) + P(V' - V) - N\beta^{-1} \ln(V'/V)]) > \mathcal{R} \, , \qquad (90)$$

where $\mathcal{R}$ is a random number, uniformly distributed over the interval $[0, 1]$. Instead of attempting random changes in the volume itself, one might construct trial moves in the box-length $L$ [17], or in the logarithm of the volume [18]. Such trial moves are equally legitimate, as long as the symmetry of the underlying Markov chain is maintained. However, such alternative schemes result in a slightly different form for eqn. 90.

Thus far we have limited our discussion of constant-pressure Monte Carlo to pure, atomic systems. Extension of the technique to mixtures is straightforward. The method is also easily applicable to molecular systems. However, in the latter case, it is crucial to note that *only the center-of-mass positions of the molecules should be scaled in a volume move*, but never the relative positions of the constituent atoms in the molecule.

## 9.2 Grand canonical ensemble

The Metropolis sampling scheme allows us to compute thermal averages of functions $A(\mathbf{r}^N)$, that depend explicitly on the coordinates of the molecules in the $N$-body system under study. Examples of such 'mechanical' properties are the potential energy or the virial contribution to the pressure. However, the Metropolis method cannot be used to determine the integral $\int d\mathbf{r}^N \exp(-\beta U(\mathbf{r}^N))$ itself. The latter quantity measures the effective volume in configuration space that is accessible to the system. Hence the original Metropolis scheme could not be used to determine those thermodynamic properties of a system that depend explicitly on the configurational integral. Examples of such 'thermal' properties are: the Helmholtz free energy $F$, the entropy $S$ and the Gibbs free energy $G$. However, although the Metropolis method cannot be used to measure, for instance, free energies directly, it can be used to measure the *difference* in free energy between two possible states of an $N$-body system. This fact is exploited in the so-called Grand-Canonical Monte Carlo method (GCMC). To simplify things, we first consider the exchange of a single molecule between an ideal gas reservoir and a medium in which $N$ other particles are present at fixed positions.

The probability of finding this molecule in an infinitesimal volume element $\mathrm{d}\mathbf{r}$ about the point $\mathbf{r}$ is proportional to $\exp[-\beta U(\mathbf{r})]\,\mathrm{d}\mathbf{r}$, where $\beta \equiv 1/k_B T$ and $U(\mathbf{r})$ is the potential energy experienced by the molecule at point $\mathbf{r}$. The molecule may either be in the gas phase, which has a (large) volume $V_0$ or in the volume $V_1$ where the other particles are. It is convenient to write the probability of finding the molecule in an infinitesimal fraction $\mathrm{d}\mathbf{s}$ of the volume of the dense medium about $\mathbf{r}$ as

$$N(\mathbf{r}) = cV_1\, e^{-\beta U(\mathbf{r})}\,\mathrm{d}\mathbf{s}, \tag{91}$$

where $c$ is a normalization constant and $\mathrm{d}\mathbf{s} \equiv \mathrm{d}\mathbf{r}/V_1$. The probability that the particle is found in an equal infinitesimal fraction of the volume of the gas is

$$N(\mathbf{r}') = cV_0\,\mathrm{d}\mathbf{s}, \tag{92}$$

where we have used the fact that $U(\mathbf{r}') = 0$ in the ideal gas. The ratio of these probabilities is

$$\frac{N(\mathbf{r})}{N(\mathbf{r}')} = \frac{V_1}{V_0}\, e^{-\beta U(\mathbf{r})}. \tag{93}$$

If we perform a Monte Carlo trial move in which we attempt to swap a particle from the ideal gas to the dense medium, we should accept this trial move with the Metropolis probability $\mathrm{acc}(0 \to 1) = \min[1, (V_1/V_0)\exp\{-\beta U(\mathbf{r})\}]$.

A single particle is not very interesting, so let us consider a system (ideal gas plus dense medium) that contains $M$ (indistinguishable) particles. The probability of finding a realization of this system where $N$ particles are in the dense medium and $M - N$ in the ideal gas is given by

$$N(\mathbf{r}^N) \propto \left(\frac{V_1^N V_0^{M-N}}{N!\,(M-N)!}\right) e^{-\beta U(\mathbf{r}^N)} \propto \left(\frac{V_1}{V_0}\right)^N \left(\frac{M!}{N!\,(M-N)!}\right) e^{-\beta U(\mathbf{r}^N)}. \tag{94}$$

We now consider the limit of an infinite ideal gas reservoir, that is, $M \to \infty$, $V_0 \to \infty$ while the density in the reservoir is fixed, $\rho = M/V_0$. Then we can rewrite eqn. 94 as

$$N(\mathbf{r}^N) \propto \frac{(\rho V_1)^N}{N!} e^{-\beta U(\mathbf{r}^N)}. \tag{95}$$

Now consider the ratio of the probabilities of finding configurations with $N+1$ and $N$ particles in the dense medium. From eqn. 95 it follows that this ratio is

$$\frac{N(\mathbf{r}^{N+1})}{N(\mathbf{r}^N)} = \frac{\rho V_1}{N+1} e^{-\beta[U(\mathbf{r}^{N+1})-U(\mathbf{r}^N)]}. \tag{96}$$

This ratio determines the acceptance probability of a Monte Carlo move in which we try to add (or remove) a particle to (from) the dense medium. Note that the properties of the reservoir enter only through the density $\rho$.

A simulation of a system in contact with an infinite particle reservoir is called a *grand canonical Monte Carlo* simulation. Usually the control parameter in such simulations is the fugacity $z$, rather than the density $\rho$, and we write

$$N_{zVT}(\mathbf{s}^N) \propto \frac{z^N V^N}{N!} e^{-\beta U(\mathbf{s}^N)}. \tag{97}$$

For an ideal gas, the fugacity is equal to the density. The relation between the fugacity and the chemical potential is

$$z = \frac{e^{\beta\mu}}{\Lambda^3}, \tag{98}$$

where $\Lambda$ is the de Broglie thermal wavelength.

In a grand canonical simulation, acceptable trial moves are

1. *Displacement of particles.* A particle is selected at random and moved to a new position. This trial move is accepted with a probability

$$\text{acc}(s \to s') = \min\Big[1, \exp\{-\beta[U(\mathbf{s'}^N) - U(\mathbf{s}^N)]\}\Big]. \tag{99}$$

2. *Insertion and removal of particles.* A particle is inserted at a random position or, with equal probability, a randomly selected particle is removed. The insertion of a particle is accepted with probability

$$\text{acc}(N \to N+1) = \min\Big[1, \frac{zV}{(N+1)} \exp\{-\beta[U(N+1) - U(N)]\}\Big] \tag{100}$$

and the removal of a particle is accepted with probability

$$\text{acc}(N \to N-1) = \min\Big[1, \frac{N}{zV} \exp\{-\beta[U(N-1) - U(N)]\}\Big]. \tag{101}$$

## 9.3 Gibbs ensemble

The condition for coexistence of two or more phases $I, II, \cdots$ is that the pressure of all coexisting phases must be equal ($P_I = P_{II} = \cdots = P$), as must be the temperature ($T_I = T_{II} = \cdots = T$) and the chemical potentials of all species ($\mu_I^\alpha = \mu_{II}^\alpha = \cdots = \mu^\alpha$). Hence one might be inclined to think that the best ensemble to study would be the 'constant-$\mu PT$ ensemble'. The quotation marks around the name of this 'ensemble' are intentional, because, strictly speaking, no such ensemble exists. The reason is simple: if we specify only intensive parameters, such as $P, T$ and $\mu$, the extensive variables (such as $V$) are unbounded. Another way to say the same thing is that the set $P, T, \mu$ is linearly dependent. In order to get a decent ensemble, we must fix at least one extensive variable. In the case of constant-pressure MC this variable is the number of particles $N$, while in Grand Canonical Monte Carlo the volume $V$ of the system is fixed.

However, we need not impose $\mu$, $P$ and $T$ individually. It suffices that in the simulation the $\mu$, $P$ and $T$ of the coexisting phases are *the same.* This condition is achieved in the Gibbs-ensemble Monte Carlo method of Panagiotopoulos [19, 20].

Let us consider the partition function for a system of $M$ particles distributed over two volumes $V$ and $V' = V_0 - V$:

$$Q(M, V, V', T) = \sum_{N=0}^{M} \frac{V^N V'^{M-N}}{\Lambda^{3M} N!(M-N)!} \int d\mathbf{s}^{M-N} \exp(-\beta U(\mathbf{s}^{M-N})) \int d\mathbf{s}^N \exp(-\beta U(\mathbf{s}^N)) \ . \tag{102}$$

We now allow trial moves to transport particles from one sub-system to the other Using the results of the previous section, it is easy to see that the probability ratio associated with a trial move that transfers one particle from volume $V'$ to volume $V$ is given by:

$$P_{N\to N+1} = \frac{V(M-N)}{V'(N+1)} \exp(-\beta[U(\mathbf{s}^{N+1}; V) - U(\mathbf{s}^N; V) + U(\mathbf{s}^{M-N-1}; V') - U(\mathbf{s}^{M-N}; V')]) \ . \tag{103}$$

The corresponding expression for the reverse trial move follows by making the appropriate substitutions in eqn. 104. As before, the acceptance or rejection of this trial move can be decided by comparing $P_{N\to N+1}$ with a random number in the interval $[0, 1]$. At this stage, we could set up a Monte Carlo simulation in which we allow trial moves that transfer particles from $V$ to $V'$ and *vice versa.* In the course of such a simulation, the distribution of particles over $V$ and $V'$ would become such that both subsystems are at the same chemical potential. This may correspond to a situation where both subsystems have the same density and pressure, but this need not be the case. For example, if the overall density of the total system ($M/V_0$), corresponds to a point in the two-phase region of a first-order phase transition, the two sub-systems may end up in different phases (which is desirable), at different pressures (which is undesirable). In order to ensure that the two subsystems are always at the same pressure, the Gibbs method also allows for volume changing moves. These may either keep the total volume $V_0$ fixed (this was the formulation of the original paper of Panagiotopoulos [19]), or the two systems may both be in contact with a constant-pressure bath at pressure $P$ (this generalization is described in a subsequent paper by Panagiotopoulos et al. [21]). Both methods follow directly from the discussion in section 9.1. For the sake of completeness we write down the expressions for the probability ratios associated with a volume-changing move in the constant-$V_0$ ensemble:

$$\begin{aligned} & P(V \to V + \Delta V, V' \to V' - \Delta V) = \\ & \quad \exp(-\beta[U_N(V + \Delta V) - U_N(V) + U_{M-N}(V' - \Delta V) - U_{M-N}(V')]). \\ & \quad \exp[N \ln((V + \Delta V)/V) + (M - N) \ln((V' - \Delta V)/V')] \; . \end{aligned} \tag{104}$$

In the constant-$P$ ensemble volume changing moves on the two subsystems can be carried out independently. The probability of acceptance of such trial moves is given directly by eqn. 90 of section 9.1. Of course, this constant-$P$ method can only be applied to systems containing two or more components because in a one-component system, the two-phase region is a *line* in the $P-T$-plane. Hence, the probabibility that any specific choice of $P$ and $T$ will actually be *at* the phase transition, is vanishingly small. In contrast, for two-component systems, the two-phase region corresponds to a finite *area* in the $P-T$-plane.

Note that in either formulation of the Gibbs method, the total number of particles is fixed. The method can be extended to study inhomogeneous systems [22] and is particularly suited to study phase equilibria in multicomponent mixtures and equilibria across semi-permeable membranes [21]. The great advantage of the Gibbs method over the conventional techniques to study phase-coexistence is that in the Gibbs method the system spontaneously ‘finds’ the densities and compositions of the coexisting phases. In contrast, the conventional approach was, for instance, to compute the relevant chemical potentials as a function of pressure at a number of different compositions (this might require an appreciable number of simulations), and then *construct* the coexistence line.

# 10 Tracing coexistence curves

Once a single point on the coexistence curve between two phases is known, the rest of that curve can be computed without further free energy calculations. A numerical technique to achieve this has been proposed by Kofke [23, 24]. In its simplest form, Kofke's method is equivalent to the numerical integration of the Clausius-Clapeyron equation (although Kofke refers to his approach as ‘Gibbs-Duhem’ integration). Let us briefly recall the derivation of the Clausius-Clapeyron equation. When two phases $\alpha$ and $\beta$ coexist at a given temperature $T$ and pressure $P$, their chemical potentials must be equal. If we change both the pressure and the temperature by infinitesimal amounts $\mathrm{d}P$ and $\mathrm{d}T$ respectively, then the difference in chemical potential of the two phases becomes

$$\mu_\alpha - \mu_\beta = -(S_\alpha - S_\beta)\mathrm{d}T + (V_\alpha - V_\beta)\mathrm{d}P \tag{105}$$

Along the coexistence curve $\mu_\alpha = \mu_\beta$, and hence

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{S_\alpha - S_\beta}{V_\alpha - V_\beta} = \frac{\Delta H}{T\Delta V} \tag{106}$$

where we have used the fact that, at coexistence, $\Delta S = T\Delta H$, where $H_\alpha$ ($H_\beta$) denotes the enthalpy of phase $\alpha$ ($\beta$). As $\Delta H$, $T$ and $\Delta V$ can all be measured directly in a simulation, $\mathrm{d}P/\mathrm{d}T$ can be computed from eqn. 106. Kofke used a predictor-corrector algorithm to solve eqn. 106. If one of the two coexisting phases is the (dilute) vapor phase, it is convenient to cast eqn. 106 in a slightly different form:

$$\frac{\mathrm{d}\ln P}{\mathrm{d}1/T} = -\frac{\Delta H}{P\Delta V/T} \tag{107}$$

Kofke and co-workers have applied this method to locate the vapor-liquid [23, 24] and solid-liquid coexistence curves of the Lennard-Jones fluid [25].

It should be stressed that Gibbs-Duhem integration is in no way limited to the computation of coexistence curves in the $P,T$–plane. A particularly important class of problems that can be treated in an analogous fashion are those where one studies the location of a phase transition as a function of the intermolecular interaction potential. For instance, Agrawal and Kofke [26] have investigated the effect of a change of the steepness of the intermolecular potential in atomic systems on the melting point. In the same spirit, Dijkstra and Frenkel studied the effect of a change in flexibility of rod-like polymers on the location of the isotropic-nematic transition [27].

Although Gibbs-Duhem integration is potentially a very efficient technique to trace a coexistence curve, it is not very robust, as it lacks built-in diagnostics. By this we mean that the numerical errors in the integration of eqn. 106 may result in large deviations of the computed coexistence points from the true coexistence curve. Similarly, any error in the location of the initial coexistence points will lead to an incorrect estimate of the coexistence curve. For this reason, it is important to check the numerical stability of the scheme. This can be achieved by performing additional free-energy calculations to fix two or more points where the two phases are in equilibrium. Recently, Meijer and Al Azhar have shown that Gibbs-Duhem integration can be made more robust by combining it with a histogram technique [28].

An alternative to Kofke's Gibbs-Duhem integration has recently been proposed by Escobedo and de Pablo [29]. The original Gibbs-Duhem integration is derived by expressing $d\mu$ as a function of $dP$ and $dT$. In the approach of Escobedo and de Pablo, the Gibbs-Duhem equation is rewritten such that it expresses $dP$ as a function of the independent varibales $d\mu$ and $dT$. At coexistence, this then yields the analog of the Clausius-Clapeyron equation:

$$\frac{d\beta\mu}{d\beta} = \frac{\rho_\alpha u_\beta - \rho_\beta u_\alpha}{\rho_\alpha - \rho_\beta} \ , \tag{108}$$

where $u_\alpha$ ($u_\beta$) denotes the molar energies of phase $\alpha$ ($\beta$). In the Gubbs-Duhem integration of ref. [29], we perform two *Grand Canonical* (rather than $NPT$) simulations in parallel. That is, we impose that the temperature and chemical potential of the two phases are equal, while eqn. 108 must ensure that the pressures of the two phases remain the same (provided that we started from a point where the phases are known to be in equilibrium). This scheme is particularly useful under conditions where particle insertions are easy, but volume moves are hard. This is a rather common situation for polymeric systems and is particularly serious for lattice systems.

# 11 Virtual moves

In the previous sections we have been discussing several Monte Carlo schemes that all aimed to sample equilibrium averages in one ensemble or another. The procedure by which this was achieved was by some kind of random walk through configuration-space, where the probability of acceptance of a trial move from one configuration to another was determined by the ratio of the probabilities of these configurations. In the present section we discuss a number of sampling schemes in which certain trial moves are attempted *but never accepted!*. I realize that such a scheme sounds very much like an exercise in futility. In fact, it is nothing of the sort, as I hope to demonstrate below.

## 11.1 Particle insertion method

Our first example of a Monte Carlo technique employing virtual moves concerns the so-called 'particle-insertion' method (often referred to as the Widom-method [30]) to measure the chemical potential $\mu$ of a species in a pure fluid or in a mixture. The statistical mechanics that is the basis for this method is quite simple. Consider the definition of the chemical potential $\mu_\alpha$ of a species $\alpha$. From thermodynamics we know that $\mu$ is defined as:

$$\begin{aligned} \mu &= \left(\frac{\partial G}{\partial N}\right)_{PT} \\ &= \left(\frac{\partial F}{\partial N}\right)_{VT} \\ &= -T\left(\frac{\partial S}{\partial N}\right)_{VE} \ . \end{aligned} \tag{109}$$

Where $G, F$ and $S$ are the Gibbs free energy, the Helmholtz free energy and the entropy, respectively. Here, and in the next few paragraphs we focus on a one-component system, and hence we drop the subscript $\alpha$. Let us first consider the situation at constant $NVT$. If we express the Helmholtz free energy of an $N$-particle system in terms of the partition function $Q_N$ (eqn. 85), then it is obvious from eqn. 109 that, for sufficiently large $N$ the chemical potential is given by: $\mu = -kT \ln(Q_{N+1}/Q_N)$. If we use the explicit form (eqn. 85) for $Q_N$, we find:

$$\begin{aligned}
\mu &= -kT \ln(Q_{N+1}/Q_N) \\
&= -kT \ln\left(\frac{V}{\Lambda^3(N+1)}\right) - kT \ln\left(\frac{\int d\mathbf{s}^{N+1} \exp(-\beta U(\mathbf{s}^{N+1})))}{\int d\mathbf{s}^N \exp(-\beta U(\mathbf{s}^N))}\right) \\
&= \mu_{id}(V) + \mu_{ex} \; . \qquad (110)
\end{aligned}$$

In the last line of eqn. 110, we have indicated the separation in the ideal-gas contribution to the chemical potential, and the excess part. As $\mu_{id}(V)$ can be evaluated analytically, we focus on $\mu_{ex}$. We now separate the potential energy of the $N+1$-particle system into the potential energy function of the $N$-particle system, $U(\mathbf{s}^N)$, and the interaction energy of the $N+1$-th particle with the rest: $\Delta U \equiv U(\mathbf{s}^{N+1}) - U(\mathbf{s}^N)$. Using this separation, we can write $\mu_{ex}$ as:

$$\mu_{ex} = -kT \ln < \int d\mathbf{s}_{N+1} \exp(-\beta \Delta U) >_N \; , \qquad (111)$$

where $< \cdots >_N$ denotes canonical ensemble averaging over the configuration space of the $N$-particle system. The important point to note is that equation 111 expresses $\mu_{ex}$ as an ensemble average that can be sampled by the conventional Metropolis scheme. There is only one aspect of this equation that makes it different form the averages that we considered before, namely the fact that we compute the average of an *integral* over the position of particle $N+1$. This last integral can be sampled by brute-force (unweighted) Monte Carlo sampling. In practice the procedure is as follows: we carry out a perfectly normal constant $NVT$ Monte Carlo simulation on the system of $N$ particles. At frequent intervals during this simulation (for instance, after every MC trial move) we randomly generate a coordinate $\mathbf{s}_{N+1}$, uniformly over the unit cube. With this value of $\mathbf{s}_{N+1}$, we then compute $\exp(-\beta\Delta U)$. By averaging the latter quantity over all generated trial positions, we obtain the average that appears in eqn. 111. So, in effect, we are computing the average of the Boltzmann factor associated with the random insertion of an additional particle in an $N$-particle system, *but we never accept any such trial insertions*, because then we would no longer be sampling the average needed in eqn. 111. The Widom method is a very powerful method to compute the chemical potential of (not too dense) atomic and simple molecular liquids. Its main advantage is its great simplicity, and the fact that it can be added on to an existing constant-$NVT$ MC program, without any modifications to the original sampling scheme: we are simply computing one more thermal average. There is something else about the Widom method that makes it appealing, but that has nothing to do with computationally efficiency: it really provides an insight into the *meaning* of the chemical potential. An insight that is often hard to extract from most text-books on statistical thermodynamics. The extension of the Widom method to other ensembles relatively straightforward.

When computing the chemical potential of chain molecules, we could use the Rosenbluth method to insert the chain. However, this method is less suited for long chains. An alternative approach is the so-called recursive sampling scheme [31, 32, 33, 34].

## 11.2 Recursive sampling

The recursive sampling approach is based on a segment-by-segment growth of the polymer. The aim is to generate a *population* of trial conformations. The excess chemical potential of a chain molecule is directly related to the average number of molecules that have survived the growth process.

The first step of the procedure is to attempt a trial insertion of a monomer in the system. Suppose that the Boltzmann factor associated with this trial insertion is $b_0 \equiv \exp[-\beta u_0(\mathbf{r}^N)]$. We now allow the monomer to make multiple copies of itself, such that the average number of copies, $< n_0 >$, is equal to

$$\langle n_0 \rangle = \pi_0 b_0$$

where $\pi_0$ is a constant multiplicative factor that remains to be specified. A convenient rule to determine how many copies should be made is the following. Denote the fractional part of $\pi_0 b_0$ by $f_0$ and the integer part by $i_0$. Our rule is then to generate $i_0$ $(i_0 + 1)$ copies of the inserted particle with a probability $1 - f_0$ $(f_0)$. Clearly if $i_0 = 0$, there is a probability $1 - f_0$ that the monomer will 'die'. Assume that we have generated at least 1 copy of the monomer. Every copy from now on proceeds independently to generate off-spring. For instance, to generate a dimer population, we add a segment to every surviving monomer. We denote the Boltzmann weight associated with these trial additions by $b_1(i)$, where the index $i$ indicates that every surviving monomer will give rise to a different dimer. As before, we have to decide how many copies of the dimers should survive. This is done in exactly the same way as for the monomer, *i.e.* the average number of dimers that descends from monomer $i$ is given by

$$\langle n_1(i) \rangle = \pi_1 b_1(i)$$

where $\pi_1$, just like $\pi_0$ before, is a constant to be specified later. The number of dimers generated may either be larger or smaller than the original number of monomers. We now proceed with the same recipe for the next generation (trimers) and so on. In practice, it is convenient to include the intra-molecular bond-bending, bond-stretching and torsional energies in the the probability distribution that determines with what orientation new segments should be added.

The average number of surviving molecules at the end of the $\ell$-th step is equal to

$$\langle N_\ell \rangle = \left( \prod_{i=0}^{\ell} \pi_i \right) \left\langle \exp[-\beta \mathcal{U}_\ell(\mathbf{r}^N)] \right\rangle$$

where $\mathcal{U}_\ell(\mathbf{r}^N)$ is the total interaction of the chain molecule with the $N$ 'solvent' molecules (and the non-bonded intra-molecular interactions). The angular brackets denote a canonical average over the coordinates and over the intra-molecular Boltzmann factors of the ideal (non-self-avoiding) chain. In other words,

$$\langle N_\ell \rangle = \left( \prod_{i=0}^{\ell} \pi_i \right) \exp[-\beta \mu_{\mathrm{ex}}(\ell)]$$

Hence, the excess chemical potential is given by

$$\mu_{ex}(\ell) = -k_{\mathrm{B}} T \ln \left( \frac{\langle N_\ell \rangle}{\prod_{i=0}^{\ell} \pi_i} \right) . \tag{112}$$

The constants $\pi_i$ should be chosen such that there is no population explosion, nor mass extinction. If we have a good guess for $\mu_{ex}(\ell)$ then we can use this to estimate $\pi_i$. In general, however, $\pi_i$ must be determined by trial and error.

This recursive algorithm has several nice features. First of all, it is computationally quite efficient (in some cases, more than an order of magnitude faster than the Rosenbluth scheme, for the same statistical accuracy). In fact, in actual calculations, the algorithm searches in *depth* first, rather than in *breadth.* That is to say: we try to grow a polymer until it has been completed (or has died). We then continue from the last 'branch' of the tree from where we are allowed to grow another trial conformation. In this way we work our way back to the 'root' of the tree. The advantage of this scheme is that the memory requirements are minimal. Moreover, the structure of the program is very simple indeed (in languages that allow recursive calls). Last but not least, the recursive scheme generates an *unbiased* (*i.e.* Boltzmann) population of chain conformations [35].

## 11.3 Exact enumeration

For lattice models, it is often possible to obtain a much more accurate estimate of the chemical potential of chain molecules. At the basis of this approach lies the fact that for non-self-avoiding polymers, we can exactly enumerate all acceptable conformations, for a given configuration of the other particles.

This is most easily seen by considering a chain of length $\ell - 1$ on a lattice. Suppose that every lattice site has $b$ neighbors, that the polymer consists of $p$ segments and that there are $N$ lattice sites. Clearly, for an ideal polymer in the absence of any obstacles, the total number of allowed conformations is $\Omega_{id} \equiv N \times b^p$. If obstacles (e.g. other particles) are present, some random walks are blocked, and the total number of allowed conformations, $\Omega_T$, is less than $\Omega_{id}$. The 'brute-force' method to determine the ratio $\Omega_T/\Omega_{id}$ would be to attempt a large number of insertions of chains with arbitrary conformation at random points on the lattice. The ratio of the number of 'accepted' trial moves to the total number of attempted insertions can be used to compute the excess chemical potential of an ideal polymer chain in this system (see section 11.1)

$$\mu_{excess} = -k_B T \log < P_{acceptance} > \tag{113}$$

However, unless the density of obstacles is quite low, the relative statistical error in the insertion probability will be quite large

Next, consider the enumeration approach [36, 37]. To this end, let us first compute all $N$ Boltzmann factors associated with the insertion of a point particle at any lattice site. Clearly, the sum of these Boltzmann factors is simply the partition function of a point-particle on a lattice, in an external potential. Let us denote the Boltzmann factor associated with site $i$ as $f_i^{(0)} \equiv \exp(-u(\mathbf{r}_i)/k_B T)$. The partition function for a one-segment polymer (2 points) is computed as follows. Starting from site $i$, we have $b$ ways to grow one segment. But all $b$ directions will, in general, have different Boltzmann weights $f_j^{(0)}$, where $j$ denotes one of the nearest neighbors of $i$. The total Boltzmann weight associated with the addition of a 1-segment polymer at site $i$ is then:

$$f_i^{(1)} \equiv f_i^{(0)} \times (\sum_j^b f_j^{(0)}) \tag{114}$$

where the sum runs over the nearest neighbors of $i$. The partition function of a 1-segment polymer on a lattice is then simply:

$$\Omega_1 = \sum_{i=1}^N f_i^{(1)}, \tag{115}$$

(where, for convenience, I have assumed that the polymer 'head' and 'tail' are distinguishable). Repeating the same argument $p$ times, it is clear that the Boltzmann factor associated with *all possible conformations* of a $p$-segment polymer starting at site $i$ is given by:

$$f_i^{(p)} = f_i^{(0)} \times (\sum_j^b f_j^{(p-1)}). \tag{116}$$

And the total partition function is given by:

$$\Omega_p = \sum_{i=1}^N f_i^{(p)}. \tag{117}$$

The important fact to note is that the computation of $\Omega_p$, a quantity that depends on $N \times b^p$ conformations, requires only $p$ iterations of $b \times N$ local 'propagations' of real numbers. For a fixed external potential, the partition function thus computed is *exact*. In a practical situation, as with the addition of polymer to a colloidal dispersion, the external potential is not fixed, but depends on the (continuous) coordinates of all $M$ colloidal particles, $\{\mathbf{r}^M\}$. Hence, the total partition function of the polymer also depends on these coordinates: $\Omega_p = \Omega_p(\mathbf{r}^M)$ and, in a simulation, we should average over a large numebr of configurations of the "bath" variables. More importantly, in many cases the assumption that the polymer is non-self-avoiding is quite unrealistic. If we take self-avoidance into account, the axact enumeration scheme described above will no longer work. However, the scheme can still be used to achieve "biased" insertion of the self-avoiding polymers. This leads to a very considerable speed up of the sampling of the insertion probability. For more details, see ref. [38].

## 11.4 Overlapping distribution method

The reader may wonder why, in the previous sections, we have only been discussing trial move that attempt to add a particle to the system, and not the reverse move. After all, the chemical potential can also be written as:

$$\begin{aligned}\mu &= +k_{\mathrm{B}}T\ln(Q_N/Q_{N+1}) \\ &= \mu_{\mathrm{id}} + k_{\mathrm{B}}T\ln\left\langle\exp(+\beta\Delta\mathcal{U})\right\rangle_{N+1} \ ,\end{aligned} \tag{118}$$

where $\Delta\mathcal{U}$ denotes the interaction energy of particle $N+1$ with the remaining $N$ particles. It would seem that equation (118) can be sampled by straightforward Metropolis Monte Carlo. In general, however, this is not true. The reason is that the function $\exp(\beta\Delta\mathcal{U})$ is, in principle, not bounded. It can become arbitrarily large, as $\Delta\mathcal{U}$ grows. (Incidentally, this is not true for $\exp(-\beta\Delta\mathcal{U})$, because one of the conditions that a system must satisfy in order to be describable by classical statistical mechanics is that its the potential energy function has a lower bound). The problem with equation (118) is that very large values of the integrand coincide with very small values $\mathcal{O}(\exp(-\beta\Delta\mathcal{U}))$ of the Boltzmann factor (that determines how often a configuration is sampled during a Monte Carlo run). As a consequence, an appreciable contribution to the average in equation (118) comes from a part of configuration space that is hardly ever, or indeed never, sampled during a run. Hard spheres offer a good illustration. As the potential energy function of non-overlapping hard spheres is always zero, a simple Monte Carlo sampling of equation (118) for a dense fluid of hard spheres would always yield the nonsensical estimate $\mu_{\mathrm{ex}} = 0$ (whereas, in fact, at freezing, $\mu_{\mathrm{ex}}/k_{\mathrm{B}}T \sim 15$). The correct way to obtain chemical potentials from simulations involving both particle insertions and particle removals has been indicated by Shing and Gubbins [85, 86]. However, we find it convenient to discuss this problem in the context of a more general technique to measure free energy differences, first introduced by Bennett [87], called the overlapping distribution method.

Consider two $N$-particle systems, labeled 0 and 1 with partition functions $Q_0$ and $Q_1$. For convenience we assume that both systems have the same volume $V$, but this is not essential. The free energy difference $\Delta F = F_1 - F_0$ can be written as:

$$\begin{aligned}\Delta F &= -k_\mathrm{B}T\ln(Q_1/Q_0)\\ &= -k_\mathrm{B}T\ln\left(\frac{\int \mathrm{d}\mathbf{s}^N \exp[-\beta\mathcal{U}_1(\mathbf{s}^N)]}{\int \mathrm{d}\mathbf{s}^N \exp[-\beta\mathcal{U}_0(\mathbf{s}^N)]}\right) . \end{aligned} \tag{119}$$

Suppose that we are carrying out a (Metropolis) sampling of the configuration space of system 1. For every configuration visited during this sampling of system 1 we can compute the potential energy of system 0 ($\mathcal{U}_0(\mathbf{s}^N)$) for the same configuration, and hence the potential energy difference $\Delta\mathcal{U} = \mathcal{U}_1(\mathbf{s}^N) - \mathcal{U}_0(\mathbf{s}^N)$. We use this information to construct a histogram that measures the probability density for the potential energy difference $\Delta\mathcal{U}$. Let us denote this probability density by $p_1(\Delta\mathcal{U})$. In the canonical ensemble, $p_1(\Delta\mathcal{U})$ is given by:

$$p_1(\Delta\mathcal{U}) = \frac{\int \mathrm{d}\mathbf{s}^N \exp(-\beta\mathcal{U}_1)\,\delta(\mathcal{U}_1 - \mathcal{U}_0 - \Delta\mathcal{U})}{q_1} , \tag{120}$$

where we have denoted the scaled, configurational part of the partition function by a lower-case $q$ (*e.g.*, $q_1 = \int \mathrm{d}\mathbf{s}^N \exp[-\beta\mathcal{U}_1(\mathbf{s}^N)]$). The $\delta$-function in equation (120) makes that we can substitute $\mathcal{U}_0 + \Delta\mathcal{U}$ for $\mathcal{U}_1$ in the Boltzmann factor, hence:

$$\begin{aligned}p_1(\Delta\mathcal{U}) &= \frac{\int \mathrm{d}\mathbf{s}^N \exp[-\beta(\mathcal{U}_0 + \Delta\mathcal{U})]\,\delta(\mathcal{U}_1 - \mathcal{U}_0 - \Delta\mathcal{U})}{q_1}\\ &= \frac{q_0}{q_1}\exp(-\beta\Delta\mathcal{U})\frac{\int \mathrm{d}\mathbf{s}^N \exp(-\beta\mathcal{U}_0)\,\delta(\mathcal{U}_1 - \mathcal{U}_0 - \Delta\mathcal{U})}{q_0}\\ &= \frac{q_0}{q_1}\exp(-\beta\Delta\mathcal{U})p_0(\Delta\mathcal{U}) , \end{aligned} \tag{121}$$

where $p_0(\Delta\mathcal{U})$ is the probability density to find a potential energy difference $\Delta\mathcal{U}$ between systems 1 and 0, while Boltzmann-sampling the available configurations of system 0. As the free energy difference between systems 1 and 0 is simply $\Delta F = -k_\mathrm{B}T\ln(q_1/q_0)$, we find from equation (121):

$$\ln p_1(\Delta\mathcal{U}) = \beta(\Delta F - \Delta\mathcal{U}) + \ln p_0(\Delta\mathcal{U}) . \tag{122}$$

In order to obtain $\Delta F$ from equation (122) in practical cases, it is convenient to define two functions $f_0$ and $f_1$ by:

$$f_0(\Delta\mathcal{U}) = \ln p_0(\Delta\mathcal{U}) - \frac{\beta\Delta\mathcal{U}}{2}$$

and

$$f_1(\Delta\mathcal{U}) = \ln p_1(\Delta\mathcal{U}) + \frac{\beta\Delta\mathcal{U}}{2}$$

such that

$$f_1(\Delta\mathcal{U}) = f_0(\Delta\mathcal{U}) + \beta\Delta F \ .$$

Suppose that we have measured $f_0$ and $f_1$ in two separate simulations (one sampling system 0, the other system 1). We can then obtain $\Delta F$ by fitting the functions $f_0$ and $f_1$ to two polynomials in $\Delta\mathcal{U}$ that are identical but for the constant term. The constant offset between the two polynomials yields our estimate for $\Delta F$. Note that, in order to perform such a fit, it is not even necessary that there exists a range of $\Delta\mathcal{U}$ where both $f_0$ and $f_1$ can be measured. However, in the absence of such a range of overlap, the statistical accuracy of the method is usually poor.

Now consider the particle insertion/removal problem. Let us assume that system 1 is a system with $N$ interacting particles, while system 0 contains $N-1$ interacting particles and 1 ideal-gas particle. The difference in free energy between these two systems is obviously equal to $\mu_{\mathrm{ex}}$. Applying equation (122) to this particular case, we find:

$$\beta\mu_{\mathrm{ex}} = f_1(\Delta\mathcal{U}) - f_0(\Delta\mathcal{U}) \ . \tag{123}$$

Equation (123) is equivalent to the result obtained by Shing and Gubbins. Using the overlapping distribution method it is possible to combine the results of simulations with trial insertions and trial removals to arrive at a more accurate estimate for the chemical potential.

## 11.5 Umbrella sampling

In the previous section, we introduced the distibution functions $p_0(\Delta U)$ and $p_1(\Delta U)$ that measure the probability of finding system 0 (1) in an equilibrium configuration $\mathbf{s}^N$ where its potential energy difference with system 1 (0) equals $\Delta U$. At first sight it would seem that knowledge of either $p_0$ or $p_1$ is sufficient to estimate the free energy difference between systems 0 and 1. After all, eqn. 122 states that

$$p_1(\Delta U) = p_0(\Delta U)\exp(\beta(\Delta F - \Delta U) \ .$$

If we integrate over $\Delta U$ on both sides of this equation, we obtain:

$$\begin{aligned} \int_{-\infty}^{\infty} p_1(\Delta U)\, d\Delta U &= \exp(\beta\Delta F)\int_{-\infty}^{\infty} p_0(\Delta U)\exp(-\beta\Delta U)\, d\Delta U \\ 1 &= \exp(\beta\Delta F) < \exp(-\beta\Delta U) >_0 \ , \end{aligned} \tag{124}$$

or

$$\exp(-\beta\Delta F) =< \exp(-\beta\Delta U) >_0 \ .$$

Although eqn. 124 is very useful to estimate free energy differences between two systems that are not too dissimilar, its applicability is limited. The problem is that, in many cases of practical interest, the largest contributions to the average

$< \exp(-\beta\Delta U) >_0$ come from region of configuration space where $p_0(\Delta U)$ is very small, while $\exp(-\beta\Delta U)$ is very large. As a result, the statistical error in $\Delta F$ is large.

One method to achieve a more accurate estimate of $\Delta F$ is the 'umbrella sampling' scheme suggested by Torrie and Valleau [39]. The basic idea behind umbrella sampling is that, in order to obtain an accurate estimate of the free energy difference between two system (0 and 1), one should sample both the part of configuration space that is accessible to system 1 and the part that is accessible to 0. In order to achieve this in a single simulation, one should modify the Markov chain that governs the sampling of configuration space. This is achieved by multiplying the Boltzmann factor of system 0 by a (positive) weighting function $w$. As a result, the probability of visiting a point $\mathbf{q}^N$ in configuration space is now proportional to $\exp(-\beta U_0(\mathbf{q}^N))w(\mathbf{q}^N)$. The expression for $< \exp(-\beta\Delta U) >_0$ now becomes:

$$< \exp(-\beta\Delta U) >_0 = \frac{\int d\mathbf{q}^N \exp(-\beta U_0(\mathbf{q}^N))w(\mathbf{q}^N)[\exp(-\beta\Delta U(\mathbf{q}^N))/w(\mathbf{q}^N)]}{\int d\mathbf{q}^N \exp(-\beta U_0(\mathbf{q}^N))w(\mathbf{q}^N)w^{-1}(\mathbf{q}^N)} \ , \tag{125}$$

or, introducing the notation $< \cdots >_w$ to denote an average over a probability distribution proportional to $\exp(-\beta U_0(\mathbf{q}^N)w(\mathbf{q}^N)$:

$$\begin{aligned} < \exp(-\beta\Delta U) >_0 &= \frac{< \exp(-\beta\Delta U)/w >_w}{< 1/w >_w} \\ &= < \exp(-\beta\Delta U)/w >_w < w >_0 \ . \end{aligned} \tag{126}$$

The second line of eqn. 126 shows that, in order for both terms on the right hand of this equation to be non-zero, $p_0(\Delta U)w$ should have an appreciable overlap with $p_1(\Delta U)$, while $w$ itself should be overlap with $p_0(\Delta U)$. This 'bridging' property of $w$ is responsible for the name 'umbrella' sampling.

Although umbrella sampling is, in principle, a powerful technique, one drawback is that the function $w$ is not known *a priori*. Rather, it must be constructed using the available information about the functions $p_0$ and $p_1$. This requires some skill. A second (though related) problem is that an unfortunate choice of $w$ may result in estimates for $\Delta F$ that appear reasonable but are, in fact, wrong. Only by systematic testing is it possible to get a feeling for the statistical errors in an umbrella sampling calculation. At first sight, it might seem advantageous to refine the computation of $w$ in such a way that *all* relevant configurations can be sampled in one run. Surprisingly, this is not the case. Rather, it is advantageous to perform several umbrella sampling runs in (partially overlapping) 'windows'. To see this, let us define an "order parameter" $\Phi$ that is a measure for the "location" of a given configuration between systems 0 and 1. For instance, $\Phi$ might be the potential energy, or the (in constant-pressure simulations) the density. Let us denote the average value of $\Phi$ in system 1 by $\Phi_{max}$ and the value in 0, by $\Phi_{min}$. Let us assume that we sample an interval $\Phi_{max} - \Phi_{min} \equiv \Delta\Phi$ in $n$ umbrella-sampling simulations. The optimum choice of $n$ is clearly the one that samples the complete $\Phi$-interval in the minimum computing time. In order to estimate this time, let us assume that the system performs a random walk in $\Phi$-space within the window $\Delta\Phi/n$. Associated with the random walk in $\Phi$-space is a 'diffusion constant' $D_\Phi$. The characteristic time needed to sample one interval $\Delta\Phi/n$ is

$$\tau_n = \frac{(\Delta\Phi/n)^2}{D_\Phi}.$$

Clearly, the total time to sample all $n$ windows is

$$\tau_{tot} = n\tau_n = \frac{(\Delta\Phi)^2}{nD_\Phi}.$$

The important point to note is that the computing time *decreases* with increasing $n$. It would, however, be incorrect to assume that $n$ should be chosen as large as possible. The actual equilibration time of a run in one of the $\Phi$-windows also depends on the rate at which all coordinates 'orthogonal' to $\Phi$ are sampled. Let us denote this time by $\tau_\perp$. Clearly, once $\tau_\perp$ becomes appreciably larger than $\tau_n$, the total computation will scale as $n \times \tau_\perp$. This suggests that the optimum choice of $n$ is the one for which $\tau_n \approx \tau_\perp$. For a more detailed discussion, see ref. [90].

The following simple example is meant to demonstrate the power of the umbrella sampling technique. Consider a model for n-butane, where all bond-lengths and bond-angles are fixed, except the torsional angle $\phi$. Let us assume that we know the intra-molecular energy function $U_{intra}(\phi)$ associated with changes of the conformation of the molecule. In the dilute gas, the probability of finding a value of the torsion angle $\phi$ is proportional to $\exp(-\beta U_{intra}(\phi))$. For n-butane, this distribution has a maximum at $\phi = 0$ (the 'trans' conformation) and two lower maxima at $\phi \approx 120$ degrees, corresponding to the 'gauche' conformation. Let us suppose that we wish to know what happens to the probability to find a molecule at the 'transition state' between the two gauche conformations, when the molecule is dissolved in an atomic liquid. The total potential energy function for the molecule plus solvent is

$$U_{tot} = U_{inter}(\mathbf{q}^N, \phi_1) + U_{intra}(\phi_1)\ .$$

The probability density $P(\phi)$ to find a particular value of the angle $\phi$ is given by:

$$P(\phi) = \frac{\int \exp(-\beta U_{tot})\delta(\phi - \phi_1)\, d\mathbf{q}^N d\phi_1}{\int \exp(-\beta U_{tot})\, d\mathbf{q}^N d\phi_1}$$

Let us now choose the weighting function $w$ equal to $\exp(+\beta U_{intra})$. With this choice, we can rewrite $P(\phi)$ as:

$$P(\phi) \quad = \quad \frac{\int \exp(-\beta U_{tot}) w(\delta(\phi - \phi_1)/w)\, d\mathbf{q}^N d\phi_1}{\int \exp(-\beta U_{tot}) w w^{-1}\, d\mathbf{q}^N d\phi_1}$$

$$
\begin{aligned}
&= \frac{\int \exp(-\beta U_{inter})(\delta(\phi-\phi_1)\exp(-\beta U_{intra})\, d\mathbf{q}^N d\phi_1}{\int \exp(-\beta U_{inter})\exp(-\beta U_{intra})\, d\mathbf{q}^N d\phi_1} \\
&= \frac{<\delta(\phi-\phi_1)\exp(-\beta U_{intra}) >_{inter}}{<\exp(-\beta U_{intra}) >_{inter}}\,. \qquad (127)
\end{aligned}
$$

But, as $U_{intra}$ depends only on $\phi$, we can rewrite eqn. 127 as:

$$P(\phi) = \frac{\exp(-\beta U_{intra}(\phi))}{<\exp(-\beta U_{intra}(\phi)) >_{inter}} P_{inter}(\phi)\ ,$$

where $P_{inter}(\phi)$ is the probability to find a conformation with internal angle $\phi$ *in the absence of the intramolecular torsion barrier.* $P_{inter}(\phi)$ can be computed accurately, even for values of $\phi$ that are very unlikely in the real system, due to the presence of the internal potential energy barrier $U_{intra}$.

# 12 Molecular Dynamics

Molecular Dynamics simulations are in many respects very similar to real experiments. When we perform a real experiment, we proceed as follows: we prepare a sample of the material that we wish to study. We connect this sample to a measuring instrument (*e.g.*, a thermometer, manometer, or viscosimeter) and we measure the property of interest during a certain time interval. If our measurements are subject to statistical noise (as most measurements are), then the longer we average, the more accurate our measurement becomes. In a Molecular Dynamics simulation, we follow exactly the same approach. First, we prepare a sample, *i.e.*, we select a model system consisting of $N$ particles and we solve Newton's equations of motion for this system until the properties of the system do not change with time anymore (we equilibrate the system). After equilibration, we perform the actual measurement. In fact, some of the most common mistakes that can be made when performing a computer experiment are very similar to the mistakes that can be made in real experiments (*e.g.*, the sample is not prepared correctly, the measurement is too short, the system undergoes an irreversible change during the experiment, or we do not measure what we think).

In order to measure an observable quantity in a Molecular Dynamics simulation, we must first of all be able to express this observable as a function of the positions and momenta of the particles in the system. For instance, a convenient definition of the temperature in a (classical) many-body system makes use of the equipartition of energy over all degrees of freedom that enter quadratically in the Hamiltonian of the system. In particular for the average kinetic energy per degree of freedom, we have:

$$\left\langle \frac{1}{2} m v_\alpha^2 \right\rangle = \frac{1}{2} k_B T \qquad (128)$$

In a simulation, we use this equation as an operational definition of the temperature. In practice, we would measure the total kinetic energy of the system, and divide this by the number of degrees of freedom $N_f (= 3N - 3$ for a system of $N$ particles with fixed total momentum[7]). As the total kinetic energy of a system fluctuates, so does the instantaneous temperature

$$T(t) = \sum_{i=1}^{N} \frac{m_i v_i^2(t)}{k_B N_f} \ . \tag{129}$$

The relative fluctuations in the temperature will be of order $1/\sqrt{N_f}$. As $N_f$ is typically of the order of $10^2$ - $10^3$, the statistical fluctuations in the temperature are of the order of 5-10 %. In order to get an accurate estimate of the temperature, one should average over many fluctuations.

# 13 Molecular Dynamics: a Program

A simple Molecular Dynamics program proceeds through the following steps:

1. We read in the parameters that specify the conditions of the run (*e.g.,* initial temperature, number of particles, density, time-step)
2. We initialize the system (*i.e.,* we select initial positions and velocities)
3. We compute the forces on all particles.
4. We integrate Newton's equations of motion. This step, and the previous one make up the core of the simulation. They are repeated until we have computed the time evolution of the system for the desired length of time.
5. After completion of the central loop, we compute and print the averages of measured quantities, and stop

Assume that the value of the density and initial temperature are chosen such that the simple cubic lattice is mechanically unstable and melts rapidly. First, we put each particle on its lattice site, and then we attribute to each velocity component of every particle a value that is drawn from a uniform distribution in the interval $[-0.5, 0.5]$. This initial velocity distribution is neither Maxwellian in shape, nor even in width. Subsequently, we shift all velocities, such that the total momentum is zero, and we scale the resulting velocities to adjust the mean kinetic energy to the desired value. We know that, in thermal equilibrium, the following relation should hold:

$$\left\langle v_\alpha^2 \right\rangle = k_B T/m \tag{130}$$

---

[7] Actually, if we define the temperature of a micro-canonical ensemble through $(k_B T)^{-1}$ = $(\partial \ln \Omega / \partial E)$, then we find that, for a $d$-dimensional system of $N$ atoms with fixed total momentum, $k_B T$ is equal to $2E/(d(N-1)-2)$.

where $v_\alpha$ is the $\alpha$-component of the velocity of a given particle. We can use this relation to define an instantaneous temperature at time $t$ $T(t)$:

$$k_B T(t) \equiv \sum_{i=1}^{\mathrm{N}} \frac{m v_{\alpha,i}^2(t)}{N_f} \,. \tag{131}$$

Clearly, we can adjust the instantaneous temperature $T(t)$ to match the desired temperature $T$ by scaling all velocities with a factor $(T/T(t))^{1/2}$. This initial setting of the temperature is not particularly critical, as the temperature will change anyway during equilibration.

As will appear later, we do not really use the velocities themselves in our algorithm to solve Newton's equations of motion. Rather, we use the positions of all particles at the present (`x`) and previous (`xm`) time steps, combined with our knowledge of the force (`f`) acting on the particles, to predict the positions at the next time step. When we start the simulation, we must bootstrap this procedure by generating approximate previous positions. Without much consideration for any law of mechanics but the conservation of linear momentum, we approximate `x` for a particle in a direction by: `xm(i) = x(i) - v(i)*dt`. Of course, we could make a better estimate of the true previous position of each particle. But as we are only bootstrapping the simulation, we do not worry about such subtleties.

## 13.1 The force calculation

What comes next is the most time-consuming part of almost all Molecular Dynamics simulations, *viz.*, the calculation of the force acting on every particle. If we consider a model system with pairwise additive interactions (as we do in the present case), we have to consider the contribution to the force on particle $i$, due to all its neighbors. If we only consider the interaction between a particle and the nearest image of another particle, this implies that, for a system of $N$ particles, we must evaluate $N \times (N-1)/2$ pair interactions.

This implies that, if we use no tricks, the time needed for the evaluation of the forces scales as $N^2$. There exist efficient techniques to speed-up the evaluation of both short-range and long-range forces in such a way that the computing time scales as $N$, rather than $N^2$.

We first compute the current distance in the $x$, $y$ and $z$ directions between each pair of particles `i` and `j`. These distances are indicated by `xr`. As in the Monte Carlo case, we use periodic boundary conditions. In the present example, we use a cut off at a distance $r_c$ in the explicit calculation of intermolecular interactions, where $r_c$ is chosen to be less than half the diameter of the periodic box. In that case we can always limit the evaluation of intermolecular interactions between `i` and `j` to the interaction between `i` and the nearest periodic image of `j`.

In the present case, the diameter of the periodic box is denoted by `box`. If we use simple cubic periodic boundary conditions, the distance in any direction between `i` and the nearest image of `j` should always be less (in absolute value) than `box/2`. A compact way to compute the distance between `i` and the nearest periodic image of `j` makes us of the nearest integer function (`nint(x)` in `FORTRAN`). The `nint` function simply rounds a real number to the nearest integer [8]. Starting with the $x$-distance (say) between `i` and any periodic image of `j`: `xr`, we compute the $x$-distance between `i` and the nearest image of `j` as, `xr=xr-box*nint(xr/box)`. Having thus computed all Cartesian components of $\mathbf{r}_{ij}$, the vector distance between `i` and the nearest image of `j`, we compute $r_{ij}^2$ (denoted by `r2` in the program). Next we test if $r_{ij}^2$ is less than $r_c^2$, the square of the cut-off radius. If not, we immediately skip to the next value of `j`. It is perhaps worth emphasizing that we do not compute $|r_{ij}|$ itself, because this would be both unnecessary and expensive (as it would involve the evaluation of a square root).

If a given pair of particles is close enough to interact, we must compute the force between these particles, and the contribution to the potential energy. Suppose that we wish to compute the $x$-component of the force:

$$\begin{aligned} f_x(r) &= -\frac{\partial u(r)}{\partial x} \\ &= -\left(\frac{x}{r}\right)\left(\frac{\partial u(r)}{\partial r}\right) . \end{aligned}$$

For a Lennard-Jones system (in reduced units),

$$f_x(r) = \frac{48x}{r^2}\left(\frac{1}{r^{12}} - 0.5\frac{1}{r^6}\right) .$$

Note that, while computing the interactions between particles, we try, as much as possible, to avoid divisions because such operations, although cheaper than the computation of a square root, are more expensive than additions, subtractions and multiplications.

## 13.2 Integrating the equations of motion

Now that we have computed all forces between the particles, we can integrate Newton's equations of motion. There are algorithms that have been designed to do this. Some of these will be discussed in a bit more detail below. In the program below, we have used the so-called Verlet algorithm. This algorithm is not only one of the simplest, but also usually the best.

To "derive" it, we start with a Taylor expansion of the coordinate of a particle, around time $t$:

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 + \frac{\Delta t^3}{3!}\dddot{r} + \mathcal{O}(\Delta t^4)$$

---

[8] Unfortunately, many FORTRAN compilers yield very slow `nint` functions. It is often cheaper to write your own code to replace the `nint` library routine.

### Algorithm 1 (Integrating the equations of motion)

```
subroutine integrate(f,en)     Integrate equations of motion
sumv=0
sumv2=0
do i=1,npart                   MD loop
   xx=2*x(i)-xm(i)*dt*f(i)     Verlet algorithm (132)
   vi=(xx-xm(i))/(2*dt)        velocity (133)
   sumv=sumv+vi                velocity center of mass
   sumv2=sumv2+vi**2           total kinetic energy
   xm(i)=x(i)                  update positions previous time step
   x(i)=xx                     update positions current time step
enddo
temp=sumv2/(3*npart)           instantaneous temperature
etot=en+sumv2/(2*npart)        total energy
return
end
```

*Comments:*

1. *the total energy* `etot` *should remain approximately constant during the simulation. A drift of this quantity may signal programming errors. It is therefore important to monitor this quantity. Similarly the velocity of the center of mass* `sumv` *should remain zero.*

2. *in this subroutine we use the Verletalgorithm (132) to integrate the equations of motion. The velocities at time step $t$ are calculated using equation (133).*

similarly,

$$r(t-\Delta t) = r(t) - v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 - \frac{\Delta t^3}{3!}\; \dddot{r} + \mathcal{O}(\Delta t^4)$$

Summing these two equations, we obtain:

$$r(t+\Delta t) + r(t-\Delta t) = 2r(t) + \frac{f(t)}{m}\Delta t^2 + \mathcal{O}(\Delta t^4)$$

or

$$r(t+\Delta t) \approx 2r(t) - r(t-\Delta t) + \frac{f(t)}{m}\Delta t^2 \,. \tag{132}$$

The estimate of the new position contains an error that is of order $\Delta t^4$, where $\Delta t$ is the time-step in our Molecular Dynamics scheme. Note that the Verlet algorithm does not use the velocity to compute the new position. One can, however, derive the velocity from knowledge of the trajectory, using:

$$r(t+\Delta t) - r(t-\Delta t) = 2v(t)\Delta t + \mathcal{O}(\Delta t^3)$$

or,

$$v(t) = \frac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t} + \mathcal{O}(\Delta t^2) \tag{133}$$

This expression for the velocity is only accurate to order $\Delta t^2$. However, it is possible to obtain more accurate estimates of the velocity (and thereby of the kinetic energy) using a Verlet-like algorithm (*i.e.*, an algorithm that yields trajectories that are identical to the one given by equation (132)). In our program, we use the velocities only to compute the kinetic energy and, thereby the instantaneous temperature.

Now that we have computed the new positions, we may discard the positions at time $t - \Delta t$. The current positions become the old positions and the new positions become the current positions.

At the end of every time-step, we compute the current temperature (`temp`), the current potential energy (`en`) which has been calculated in the force loop, and the total energy (`etot`). Note that the total energy should be conserved.

This completes the introduction to the Molecular Dynamics method. The reader should now be able to write a basic Molecular Dynamics program for liquids or solids consisting of spherical particles. In what follows, we shall do two things: first of all, we discuss in a bit more detail, the methods that are available to integrate the equations of motion. Next, we discuss measurements in Molecular Dynamics simulations.

# 14 Algorithms

It is obvious that a good Molecular Dynamics program requires a good algorithm to integrate Newton's equations of motion. In this sense, the choice of algorithm is crucial. However, although it is easy to recognize a *bad* algorithm, it is not immediately obvious what criteria a *good* algorithm should satisfy.

Let us look at the different points to consider.

1. **Speed**. Although, at first sight, this seems important, it is usually not very relevant because the fraction of the time spend on integrating the equations of motion (as opposed to computing the interactions) is small, at least for atomic and simple molecular systems.

2. **Accurate for large time steps**. This is more important, because the longer the time-step that we can use, the fewer evaluations of the forces are needed per unit of simulation time. Hence, this would suggest that it is advantageous to use a sophisticated algorithm that allows one to use a long time step.

3. **Memory**. However, as we shall see below, algorithms that allow one to use a large time-step, achieve this by storing information on increasingly higher-order derivatives of the particle coordinates. As a consequence, they tend to require more storage. For a typical simulation, this is usually not a serious drawback because, unless one considers very large systems, the amount of memory needed to store these derivatives is small compared to the total amount available even on a normal workstation.

4. **Energy conservation**. This is an important criterion, but actually we should distinguish two kinds of energy conservation, *viz.*, short-time and long-time. The sophisticated higher-order algorithms tend to have very good energy conservation for short times (*i.e.*, during a few time-steps). However, they often have the undesirable feature that the overall energy drifts for long times. In contrast, Verlet-style algorithms tend to have only moderate short-term energy conservation, but little long-term drift.

5. **Accuracy**. It would seem to be most important to have an algorithm that accurately predicts the trajectory of all particles for both short and long times. In fact, no such algorithm exists. For essentially all systems that we study by MD simulations, we are in the regime where the trajectory of the system through phase space (*i.e.*, the $6N$-dimensional space spanned by all particle coordinates and momenta) depends sensitively on the initial conditions. This means that two trajectories that are initially very close, will diverge exponentially as time progresses. We can consider the integration error caused by the algorithm as the source for the initial small difference between the 'true' trajectory of the system and the trajectory that is generated in our simulation. We should expect that any integration error, no matter how small, will always cause our simulated trajectory to diverge exponentially from the true trajectory compatible with the same initial conditions. This so-called Lyapunov instability (see section 14.2) would seem to be a

devastating blow to the whole idea of Molecular Dynamics simulations but we have good reasons to assume that even this problem need not be serious. Clearly, this statement requires some clarification. First of all, one should realize that the aim of an MD simulation is *not* to predict precisely what will happen to a system that has been prepared in an precisely known initial condition: we are always interested in statistical predictions. We wish to predict the average behavior of a system that was prepared in an initial state about which we know something (*e.g.*, the total energy) but by no means everything. In this respect, MD simulations differ fundamentally from numerical schemes to predict the trajectory of satellites through space: in the latter case, we really wish to predict the true trajectory. We cannot afford to launch an ensemble of satellites and make statistical predictions about their destination. However, in MD simulations, statistical predictions are good enough. Still, this would not justify the use of inaccurate trajectories unless the trajectories obtained numerically are, in some sense, close to true trajectories. It is this latter statement that is generally believed to be true although, to our knowledge, it has not been proven for any class of systems that is of interest for MD simulations. However, there is considerable numerical evidence (see *e.g.*, [40]) that there exist so-called shadow orbits. A shadow orbit is a true trajectory of a many-body system that closely follows the numerical trajectory for a time that is long compared to the time it takes the Lyapunov instability to develop. Hence the results of our simulation are representative of a true trajectory in phase space, even though we cannot tell a priori which. Surprisingly (and fortunately) it appears that shadow orbits are better behaved (*i.e.*, track the numerical trajectories better) for systems in which small differences in the initial conditions lead to an exponential divergence of trajectories than for the, seemingly simpler systems that show no such divergence [40]. In spite of this reassuring evidence, it should be emphasized that it is just evidence and no proof. Hence our trust in Molecular Dynamics simulation as a tool to study the time evolution of many-body systems is largely based on belief. To conclude this discussion, let us say that there is clearly still a corpse in the cupboard. We believe this corpse will not haunt us, and we quickly close the cupboard. For more details, the reader is referred to [41, 42].

6. **Reversibility and area preservation**. Newton's equation of motion are time-reversible, and so should be our algorithms. In fact, many algorithms are *not* time reversible. That is, future and past phase-space coordinates do not play a symmetric role in such algorithms. As a consequence, if one were to reverse the momenta of all particles at a given instant, the system would not trace back its trajectory in phase space, even if the simulation would be carried out with infinite numerical precision. Only in the limit of an infinitely short time-step will such algorithms become reversible. However,

what is more important, many seemingly reasonable algorithms differ in another crucial respect from Hamilton's equation of motion: true Hamiltonian Dynamics leaves the magnitude of any volume-element in phase space unchanged, but many numerical schemes, in particular those that are not time-reversible, do not reproduce this area-preserving property. This may sound like a very esoteric objection to an algorithm, but it is not. Again, without attempting to achieve a rigorous formulation of the problem, let us simply note that all trajectories that correspond to a particular energy $E$ are contained in a (hyper)-volume $\Omega$ in phase space. If we let Hamilton's equation of motion act on all points in this volume (*i.e.*, we let the volume evolve in time), then we end up with exactly the same volume. However, a non-area-preserving algorithm will map the volume $\Omega$ on another (usually larger) volume $\Omega'$. After sufficiently long times, we expect that the non-area-preserving algorithm will have greatly expanded the volume of our system in phase space. This is not compatible with energy conservation. Hence it is plausible that non-reversible algorithms will have serious long-term energy drift problems. Reversible, area-preserving algorithms will not change the magnitude of the volume in phase space. This property is not sufficient to guarantee the absence of long-term energy drift, but it is at least compatible with it. It is possible to check whether an algorithm is area preserving by computing the Jacobian associated with the transformation of old to new phase-space coordinates.

Finally, it should be noted that even when we integrate a time-reversible algorithm, we shall find that the numerical implementation is hardly ever truly time-reversible. This is so, because we work on a computer with finite machine precision using floating point arithmetic that results in rounding errors (of the order of the machine precision).

In the remainder of this chapter, we shall discuss most of the above points in more detail. Before we do so, let us first consider how the Verlet algorithm scores on the points listed above. First of all, the Verlet algorithm is fast. But we had argued that this is relatively unimportant. Secondly, it is not particularly accurate for long time steps. Hence, we should expect to compute the forces on all particles rather frequently. Thirdly, it requires about as little memory as is at all possible. This is useful when we simulate very large systems, but in general it is not a crucial advantage. Fourthly, its short term energy conservation is fair (in particular in the versions that use a more accurate expression for the velocities) but, more importantly, it exhibits little long-term energy drift. This is related to the fact that the Verlet algorithm is time-reversible and area-preserving. In fact, although the Verlet algorithm does not conserve the total energy of this system exactly, there is strong evidence that it does conserve a pseudo-Hamiltonian that approaches the true Hamiltonian in the limit of infinitely short time-steps (see section 14.1). The accuracy of the trajectories generated with the Verlet algorithm is not impressive. But then, it would hardly help to use a better algorithm. Such an algorithm may postpone the unavoidable exponential growth of the error in the trajectory by a few hundred time-steps (see section 14.2). But no algorithm is good enough that it will keep the trajectories close to the true trajectories for a time comparable to the duration of a typical Molecular Dynamics run[9].

## 14.1 Liouville formulation of time-reversible algorithms.

Thus far, we have considered algorithms to integrate Newton's equations of motion from the point of view of applied mathematics. However, recently Tuckerman, Berne and Martyna [43] have shown how to systematically derive time-reversible, area-preserving MD algorithms from the Liouville formulation of classical mechanics. The same approach has been developed independently by Sexton and Weingarten [44], in the context of hybrid Monte Carlo simulations. As the Liouville formulation provides considerable insight into what makes an algorithm a good algorithm, we briefly review the Liouville approach.

Let us consider an arbitrary function $f$ that depends on all the coordinates and momenta of the $N$ particles in a classical many-body system. $f(\mathbf{p}^N(t), \mathbf{r}^N(t))$ depends on the time $t$ implicitly, *i.e.*, through the dependence of $(\mathbf{p}^N, \mathbf{r}^N)$ on $t$. The time derivative of $f$ is $\dot{f}$:

$$\begin{aligned} \dot{f} &= \dot{\mathbf{r}}\frac{\partial f}{\partial \mathbf{r}} + \dot{\mathbf{p}}\frac{\partial f}{\partial \mathbf{p}} \\ &\equiv \mathrm{i}Lf \end{aligned} \tag{134}$$

where we have used the shorthand notation $\mathbf{r}$ for $\mathbf{r}^N$ and $\mathbf{p}$ for $\mathbf{p}^N$. The last line of equation (134) defines the Liouville operator

$$\mathrm{i}L = \dot{\mathbf{r}}\frac{\partial}{\partial \mathbf{r}} + \dot{\mathbf{p}}\frac{\partial}{\partial \mathbf{p}} \tag{135}$$

We can formally integrate equation (134) to obtain

$$f\left(\mathbf{p}^N(t), \mathbf{r}^N(t)\right) = \exp(\mathrm{i}Lt) f\left(\mathbf{p}^N(0), \mathbf{r}^N(0)\right) \tag{136}$$

In all cases of practical interest, we cannot do much with this formal solution, because evaluating the right hand side is still equivalent to the exact integration of the classical equations of motion. However, there are a few simple cases for which the formal solution is known explicitly. In particular, suppose that our Liouville operator contained only the first term on the right-hand side of equation (134). We denote this part of i$L$ by i$L_r$.

$$\mathrm{i}L_r \equiv \dot{\mathbf{r}}(0)\frac{\partial}{\partial \mathbf{r}} \ , \tag{137}$$

---

[9] Error free integration of the equations of motion is possible for certain discrete models, such as lattice-gas cellular automata. But these models do not follow Newton's equation of motion.

where $\dot{\mathbf{r}}(0)$ is the value of $\dot{\mathbf{r}}$ at time $t{=}0$. If we insert $\mathrm{i}L_r$ in equation (136) and use a Taylor expansion of the exponential on the right hand side, we get

$$\begin{aligned} f(t) &= f(0) + \mathrm{i}L_r t f(0) + \frac{(\mathrm{i}L_r t)^2}{2!} f(0) + \cdots \\ &= \exp\left(\dot{\mathbf{r}}(0) t \frac{\partial}{\partial \mathbf{r}}\right) f(0) \\ &= \sum_{n=0}^{\infty} \frac{(\dot{\mathbf{r}}(0)t)^n}{n!} \frac{\partial^n}{\partial \mathbf{r}^n} f(0) \\ &= f\left(\mathbf{p}^N(0), (\mathbf{r} + \dot{\mathbf{r}}(0)t)^N\right) \end{aligned} \tag{138}$$

Hence the effect of $\exp(\mathrm{i}L_r t)$ is a simple shift of coordinates. Similarly, the effect of $\exp(\mathrm{i}L_p t)$, with $\mathrm{i}L_p$ defined as

$$\mathrm{i}L_p \equiv \dot{\mathbf{p}}(0) \frac{\partial}{\partial \mathbf{p}} \, , \tag{139}$$

is a simple shift of momenta. The total Liouville operator, $\mathrm{i}L$ is equal to $\mathrm{i}L_r + \mathrm{i}L_p$. Unfortunately, we cannot replace $\exp(\mathrm{i}Lt)$ by $\exp(\mathrm{i}L_r t) \times \exp(\mathrm{i}L_p t)$, because $\mathrm{i}L_r$ and $\mathrm{i}L_p$ are non-commuting operators. For non-commuting operators $A$ and $B$, we have

$$\exp(A + B) \neq \exp(A) \exp(B) \, . \tag{140}$$

However, we do have the following (Trotter) identity:

$$e^{(A+B)} = \lim_{P\to\infty} \left(e^{\frac{A}{2P}} e^{\frac{B}{P}} e^{\frac{A}{2P}}\right)^P \tag{141}$$

In the limit $P \to \infty$, this relation is formally correct, but of limited practical value. However, for large but finite $P$, we have

$$e^{(A+B)} = \left(e^{\frac{A}{2P}} e^{\frac{B}{P}} e^{\frac{A}{2P}}\right)^P e^{\mathcal{O}(1/P^2)} \tag{142}$$

Now let us apply the above expression to the formal solution of the Liouville equation. To this end, we make the identification

$$\frac{A}{P} \equiv \frac{\mathrm{i}L_p t}{P} \equiv \Delta \dot{\mathbf{p}}(0) \frac{\partial}{\partial \mathbf{p}}$$

and

$$\frac{B}{P} \equiv \frac{\mathrm{i}L_r t}{P} \equiv \Delta \dot{\mathbf{r}}(0) \frac{\partial}{\partial \mathbf{r}}$$

where $\Delta = t/P$. The idea is now to replace the formal solution of the Liouville equation by the discretized version, equation (142). In this scheme, one time-step corresponds to applying the operator

$$\mathrm{e}^{\frac{\mathrm{i}L_p \Delta}{2}} \mathrm{e}^{\mathrm{i}L_r \Delta} \mathrm{e}^{\frac{\mathrm{i}L_p \Delta}{2}}$$

once. Let us see what the effect is of this operator on the coordinates and momenta of the particles. First, we apply $\exp(\mathrm{i}L_p\Delta/2)$ to $f$ and obtain

$$\mathrm{e}^{\frac{\mathrm{i}L_p\Delta}{2}} f\left(\mathbf{p}^N(0),\mathbf{r}^N(0)\right) = f\left((\mathbf{p}(0)+\frac{\Delta}{2}\dot{\mathbf{p}}(0))^N,\mathbf{r}^N(0)\right)$$

Next, we apply $\exp(\mathrm{i}L_r\Delta)$ to the result of the previous step

$$\mathrm{e}^{\mathrm{i}L_r\Delta} f\left((\mathbf{p}(0)+\frac{\Delta}{2}\dot{\mathbf{p}}(0))^N,\mathbf{r}^N(0)\right) = \\ f\left((\mathbf{p}(0)+\frac{\Delta}{2}\dot{\mathbf{p}}(0))^N,(\mathbf{r}(0)+\Delta\dot{\mathbf{r}}(\Delta/2))^N\right)$$

and finally, we apply $\exp(\mathrm{i}L_p\Delta/2)$ once more, to obtain

$$f\left((\mathbf{p}(0)+\frac{\Delta}{2}\dot{\mathbf{p}}(0)+\frac{\Delta}{2}\dot{\mathbf{p}}(\Delta))^N,(\mathbf{r}(0)+\Delta\dot{\mathbf{r}}(\Delta/2))^N\right)$$

Note that every step in the above sequence corresponds to a simple shift operation in either $\mathbf{r}^N$ or $\mathbf{p}^N$. It is of particular importance to note that the shift in $\mathbf{r}$ is a function of $\mathbf{p}$ only (because $\dot{\mathbf{r}}$=$\mathbf{p}/m$), while the shift in $\mathbf{p}$ is a function of $\mathbf{r}$ only (because $\dot{\mathbf{p}}$=$\mathbf{F}(\mathbf{r}^N)$). The Jacobian of the transformation from $\{\mathbf{p}^N(0),\mathbf{r}^N(0)\}$ to $\{\mathbf{p}^N(\Delta),\mathbf{r}^N(\Delta)\}$ is simply the product of the Jacobians of the three elementary transformations. But as each of these Jacobians is equal to one, the overall Jacobian is also equal to one. In other words, the algorithm is area preserving.

If we now consider the overall effect of this sequence of operations on the positions and momenta, we find the following:

$$\begin{aligned}\mathbf{p}(0) &\rightarrow \mathbf{p}(0)+\frac{\Delta}{2}\left(\mathbf{F}(0)+\mathbf{F}(\Delta)\right) && (143)\\ \mathbf{r}(0) &\rightarrow \mathbf{r}(0)+\Delta\dot{\mathbf{r}}(\Delta/2) \\ &= \mathbf{r}(0)+\Delta\dot{\mathbf{r}}(0)+\frac{\Delta^2}{2}\mathbf{F}(0) && (144)\end{aligned}$$

But these are precisely the equations of the Verlet algorithm (in the velocity form). Hence, we have shown that the Verlet algorithm is area preserving. The fact that it is reversible follows directly from the fact that past and future coordinates enter symmetrically in the algorithm.

The method of ref. [43] allows us to derive the Verlet algorithm as a special case of the Trotter expansion of the time-evolution operator. It should be realized that the decomposition of $\mathrm{i}L$ as a sum of $\mathrm{i}L_r$ and $\mathrm{i}L_p$ is arbitrary. Other decompositions are possible and may lead to algorithms that are more convenient.

Finally, let us try to understand the absence of long-term energy drift in the Verlet algorithm. When we use the Verlet algorithm, we replace the true Liouville operator $\exp(\mathrm{i}Lt)$ by $\exp(\mathrm{i}L_r\Delta t/2)\exp(\mathrm{i}L_P\Delta t)\exp(\mathrm{i}L_r\Delta t/2)$. In doing so, we make an error. If all (n-th order) commutators of $L_p$ and $L_r$ exist (*i.e.*, if the

Hamiltonian is an infinitely differentiable function of $\mathbf{p}^N$ and $\mathbf{r}^N$) then we can, at least in principle, evaluate the error that is involved in this replacement:

$$\exp(\mathrm{i}L_r\Delta t/2)\exp(\mathrm{i}L_P\Delta t)\exp(\mathrm{i}L_r\Delta t/2) = \exp(\mathrm{i}L\Delta t + \epsilon) \tag{145}$$

where $\epsilon$ is an operator that can be expressed in terms of the commutators of $L_p$ and $L_r$

$$\epsilon = \sum_{n=1}^{\infty} (\Delta t)^{2n+1} c_{2n+1} \tag{146}$$

where $c_m$ denotes a combination of $m$-th order commutators. For instance, the leading term is

$$-(\Delta t)^3 \left( \frac{1}{24}[\mathrm{i}L_r,[\mathrm{i}L_r,\mathrm{i}L_p]] + \frac{1}{12}[\mathrm{i}L_p,[\mathrm{i}L_r,\mathrm{i}L_p]] \right) \ .$$

Now the interesting thing to note is that, if the expansion in equation (146) converges, then we can define a pseudo Liouville operator

$$\mathrm{i}L_{\mathrm{pseudo}} \equiv \mathrm{i}L + \epsilon/\Delta t \ .$$

This pseudo Liouville operator corresponds to a pseudo Hamiltonian and the remarkable thing is that this pseudo Hamiltonian ($H_{\mathrm{pseudo}}$) is rigorously conserved by Verlet style (or generalized multi-time-step) algorithms [45, 46, 47]. The difference between the conserved pseudo Hamiltonian and the true Hamiltonian of the system is of order $(\Delta t)^{2n}$ (where $n$ depends on the order of the algorithm). Clearly, by choosing $\Delta t$ small (and, if necessary, $n$ large), we can make the difference between the true and the pseudo Hamiltonian as small as we like. As the true Hamiltonian is forced to remain close to a conserved quantity, we can now understand why there is no long term drift in the energy with Verlet-style algorithms. In some cases, we can explicitly compute the commutators (for instance, for a harmonic system) and can verify that the pseudo-Hamiltonian is indeed conserved [41]. And even if we cannot compute the complete series of commutators, the leading term will give us an improved estimate of the pseudo-Hamiltonian. Toxvaerd [41] has verified that even for a realistic many-body system, such an approximate pseudo-Hamiltonian is very nearly a constant of motion.

## 14.2 Lyapunov instability

To end this discussion of algorithms, we wish to illustrate the extreme sensitivity of the trajectories to small differences in initial conditions. Let us consider the position ($\mathbf{r}^N$) of one of the $N$ particles at time $t$. This position is a function of the initial positions and momenta at $t = 0$:

$$\mathbf{r}(t) = f(\mathbf{r}^N(0), \mathbf{p}^N(0); t)$$

Let us now consider the position at time $t$ that would result if we perturbed the initial conditions (say, some of the momenta) by a small amount $\epsilon$. In that case, we would obtain a different value for $r$ at time $t$:

$$\mathbf{r}'(t) = f(\mathbf{r}^N(0), \mathbf{p}^N(0) + \epsilon; t)$$

We denote the difference between $\mathbf{r}(t)$ and $\mathbf{r}'(t)$ by $\Delta\mathbf{r}(t)$. For sufficiently short times, $\Delta\mathbf{r}(t)$ is linear in $\epsilon$. However, the coefficient of the linear dependence diverges exponentially, *i.e.*,

$$|\Delta\mathbf{r}(t)| \sim \epsilon \exp(\lambda t) \tag{147}$$

This so-called Lyapunov instability of the trajectories is responsible for the fact that we cannot hope to accurately predict a trajectory for all but the shortest simulations. The exponent $\lambda$ is called the Lyapunov exponent (more precisely, the largest Lyapunov exponent: there are more such exponents (6N, in fact), but the largest dominates the long-time exponential divergence of initially close trajectories). Suppose that we wish to maintain a certain bound $\Delta_{\max}$ on $|\Delta\mathbf{r}(t)|$, in the interval $0 < t < t_{\max}$. How large an initial error ($\epsilon$) can we afford? From equation (147), we deduce

$$\epsilon \sim \Delta_{\max} \exp(-\lambda t_{\max})$$

Hence, the acceptable error in our initial conditions decreases exponentially with $t_{max}$, the length of the run. To illustrate that this effect is real, we show the result of two almost identical simulations: the second differs from the first in that the $x$-components of the velocities of 2 particles (out of 1000) have been changed by $+10^{-10}$ and $-10^{-10}$ (in reduced units). We monitor the sum of the squares of the differences of the positions of all particles:

$$\sum_{i=1}^{N} |\mathbf{r}_i(t) - \mathbf{r}'_i(t)|^2$$

As can be seen in figure 2, this measure of the distance does indeed grow exponentially with time. After 1000 time-steps, the two systems that were initially very close have become very nearly uncorrelated. It should be stressed this run was performed using perfectly normal parameters (density, temperature, time-step). The only unrealistic thing about this simulation is that it is extremely short. Most Molecular Dynamics simulations require many tens, if not hundreds, of thousands of time-steps.

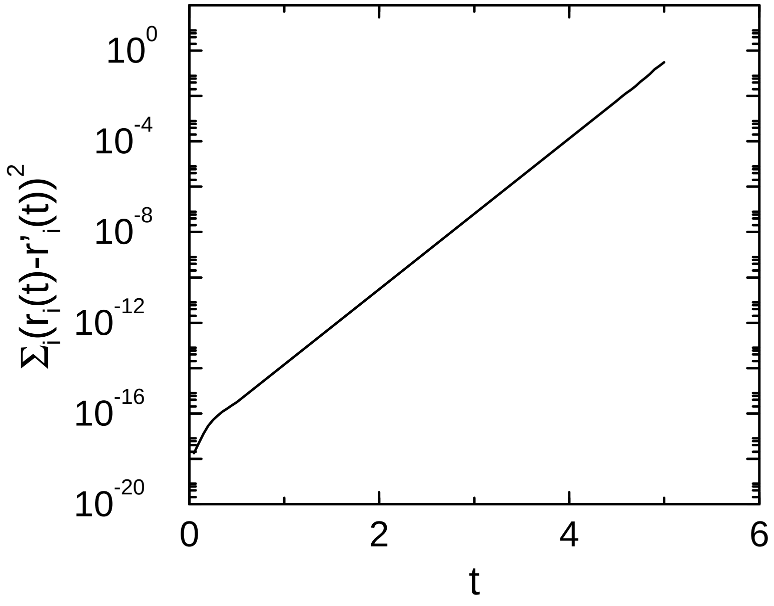

Figure 2: Illustration of the Lyapunov instability in a simulation of a Lennard-Jones system. The figure shows the time dependence of the sum of squared distances between two trajectories that were initially very close (see text). The total length of the run in reduced units was 5, which corresponds to 1000 time steps. Note that, within this relatively short time, the two trajectories become esentially uncorrelated.

# 15 Free energy and phase behavior

## 15.1 Thermodynamic Integration

The second law of thermodynamics states that for a closed system with energy $E$, volume $V$ and number of particles $N$, the entropy $S$ is at a maximum when the system is in equilibrium. From this formulation of the second law it is simple to derive the corresponding equilibrium conditions for systems that can exchange heat, particles or volume with a reservoir. In particular, if a system is in contact with a heat bath, such that its temperature $T$, volume $V$ and number of particles $N$ are fixed, then the Helmholtz free energy $F \equiv E - TS$ is at a *minimum* in equilibrium. Analogously, for a system of $N$ particles at constant pressure $P$ and temperature $T$, the Gibbs free energy $G \equiv F + PV$ is at a minimum.

If we wish to know which of two phases (denoted by $\alpha$ and $\beta$) is stable at a given temperature and density, we should simply compare the Helmholtz free energies $F_\alpha$ and $F_\beta$ of these phases. It would seem that the obvious thing to do is simply to measure $F_\alpha$ and $F_\beta$ by computer simulation. Unfortunately, it is not possible to measure the free energy (or entropy) directly in a simulation. What we *can* measure in a simulation are averages of *mechanical* quantities, *i.e.* averages of functions of the coordinates and momenta of the molecules in the system, such as the pressure or the dielectric constant. If we denote such a mechanical quantity by $A(\mathbf{p}^N, \mathbf{q}^N)$, then the average of $A$ that can be measured in a simulation at constant $N$, $V$ and $T$ is

$$< A >_{NVT} = \frac{\int d\mathbf{p}^N d\mathbf{q}^N A(\mathbf{p}^N, \mathbf{q}^N) \exp\left(-\beta H(\mathbf{p}^N, \mathbf{q}^N)\right)}{\int d\mathbf{p}^N d\mathbf{q}^N \exp\left(-\beta H(\mathbf{p}^N, \mathbf{q}^N)\right)} \tag{148}$$

where $H$ is the Hamiltonian of the system expressed as a function of the momenta $\mathbf{p}^N$ and coordinates $\mathbf{q}^N$. $k_B$ is Boltzmann's constant and $\beta = 1/(k_B T)$.

However, entropy, free energy and related quantities are not simply averages of functions of the phase-space coordinates of the system. Rather they are directly related to the *volume* in phase space that is accessible to a system. For instance, in classical statistical mechanics, the Helmholtz free energy $F$ is directly related to the canonical partition function $Q_{NVT}$:

$$F = -k_B T \ln Q_{NVT} \equiv -k_B T \ln \left( \frac{\int d\mathbf{p}^N d\mathbf{q}^N \exp\left(-\beta H(\mathbf{p}^N, \mathbf{q}^N)\right)}{h^{dN} N!} \right) \tag{149}$$

where $h$ is Planck's constant and $d$ is the dimensionality of the system.

It is clear that $Q_{NVT}$ is not of the form of a canonical average over phase space. And this is why $F$ or, for that matter, $S$ or $G$, cannot be measured directly in a simulation. We call such quantities that depend directly on the available volume in phase *thermal* quantities.

Actually, there is nothing strange about the fact that thermal quantities cannot be measured directly in a simulation: the same problem occurs in the real world – thermal quantities cannot be measured directly.

When considering numerical schemes to determine the free energy, it is therefore instructive to look at the *experimental* techniques to determine entropies or free energies. In experiments, one does not measure the free energy directly, but rather a derivative of the free energy with respect to volume $V$ or temperature $T$:

$$\left(\frac{\partial F}{\partial V}\right)_{NT} \;=\; -P \tag{150}$$

and

$$\left(\frac{\partial F/T}{\partial 1/T}\right)_{VT} \;=\; E\;. \tag{151}$$

As the pressure $P$ and the energy $E$ are mechanical quantities, they *can* be measured both in experiment and in simulation. In order to compute the free energy of a system at given temperature and density, we should find a reversible path in the $V-T$ plane, that links the state under consideration to a state of known free energy. The change in $F$ along that path can then simply be evaluated by integration of Eqns. 150 and 151. There are only very few thermodynamic states where the free energy of a substance is known. One state is the ideal gas phase, another may be the perfectly ordered ground state at $T=0K$.

In computer simulations, the situation is quite similar. In order to compute the free energy of a dense liquid, one may construct a reversible path to the very dilute gas phase. It is not really necessary to go all the way to the ideal gas. But at least one should reach a state that is sufficiently dilute that the free energy can be computed accurately, either from knowledge of the first few terms in the virial expansion of the compressibility factor $PV/(NkT)$, or that the chemical potential can be computed by other means. For the solid, the ideal gas reference state is less useful (although techniques have been developed to construct a reversible path from a dense solid to a dilute (lattice) gas [48]). The obvious reference state for solids is the harmonic lattice. Computing the absolute free energy of a harmonic solid is relatively straightforward, at least for atomic and simple molecular solids. However, not all solid phases can be reached by a reversible route from a harmonic reference state. For instance, in molecular systems it is quite common to find a strongly anharmonic plastic phase just below the melting line. This plastic phase is not (meta-) stable at low temperatures.

### 15.1.1 Artificial paths

Fortunately, in computer simulations we do not have to rely on the presence of a 'natural' reversible path between the phase under study and a reference state of known free energy. If such a path does not exist, we can construct an artificial path. This is in fact a standard trick in statistical mechanics (see e.g. [49]). It works as follows: Consider a case where we need to know the free energy $F(V,T)$ of a system with a potential energy function $U_1$, where $U_1$ is such that no 'natural' reversible path exists to a state of known free energy. Suppose now that we can find another model system with a potential energy function $U_0$ for which the free energy *can* be computed exactly. We define a generalized potential energy function $U(\lambda)$, such that $U(\lambda = 0) = U_0$ and $U(\lambda = 1) = U_1$. The free energy of a system with this generalized potential is denoted by $F(\lambda)$. Although $F(\lambda)$ itself cannot be measured directly in a simulation, we can measure its derivative with respect to $\lambda$:

$$\left(\frac{\partial F}{\partial \lambda}\right)_{NVT\lambda} = \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{NVT\lambda} \tag{152}$$

If the path from $\lambda = 0$ to $\lambda = 1$ is reversible, we can use eq. 152 to compute the desired $F(V,T)$. We simply measure $< \partial U/\partial\lambda >$ for a number of values of $\lambda$ between 0 and 1.

In the numerical simulation of bio-molecular molecules, ‘artificial’ thermodynamic integration is often used to compute the difference in excess free-energy of similar but distinct molecules (see e.g. [50]). Such calculations are important in many different contexts. For instance, one can thus compute the relative binding strengths of closely related molecules to an enzyme. In such calculations, the thermodynamic integration involves a gradual replacement of part of the molecule by another building block (for instance, an $H$ could be transformed into a $CH_3$ group).

### 15.1.2 Reference systems

Let us consider the computation of the free energy of a crystalline solid by thermodynamic integration. In such calculations it is important to select a reasonable reference system, *i.e.* a system that is, in some sense ‘close’ to the system of interest, and can be reached without crossing any first-order phase-transition boundaries. One of the safest choices for a reference system appears to be an Einstein crystal with the same structure as the phase under study [51]. This choice of reference system makes it extremely improbable that the path connecting $\lambda = 0$ and $\lambda = 1$ will cross an (irreversible) first order phase transition from the initial structure to another, only to go back to its original structure for still larger values of $\lambda$. Nevertheless, it is important that the parametrization of $U(\lambda)$ be chosen carefully. Usually, a linear parametrization (i.e. $U(\lambda) = \lambda U_1 + (1-\lambda)U_0$ ) is quite satisfactory. But occasionally such a parametrization may lead to weak (and relatively harmless) singularities in eq. 152 for $\lambda \to 0$. There are, however, alternative thermodynamic integration schemes that do not suffer from this problem [52]. More details about such free energy computations can be found in ref. [52, 77, 53].

Similar techniques can be used to locate first-order phase transitions involving phases with partial order (e.g. liquid crystals). For details, the reader is referred to refs [54, 55, 56, 57, 58, 59]. Finally, thermodynamic integration techniques are particularly useful to compute the Gibbs free energy of mixtures. An example is the work of Kranendonk and Frenkel, who have computed the melting curve of a substitutionally disordered solid mixture of hard spheres with different size [60]. In this case, thermodynamic integration is used to slowly change the size-ratio of the particles at fixed volume fraction. The reference point is size ratio $\alpha = 1$ ('isotopic mixture'). The reversible work needed to change the size ratio from 1 to a given value of $\alpha$ is a direct measure for the excess free energy of the solid solution at that composition. This technique was subsequently used by Eldridge et al. [61] to compute the relative stability of the $AB_2$ and $AB_{13}$ crystal phases of dissimilar hard spheres with a size ratio $\alpha \approx 0.58$. For details, the reader is referred to ref. [62, 63, 64].

# 16 Perturbation Theory

The thermodynamic integration scheme discussed in the previous section lies at the root of thermodynamic perturbation theory [49]. The aim of thermodynamic perturbation theory is to arrive at an estimate of the free energy (and all derived properties) of a many-body system, using as input information about the free energy and structure of a simpler reference system. We assume, as before that the potential energy function of this reference system is denoted by $U_0$ while the potential energy function of the system of interest is denoted by $U_1$. In order to compute the free energy difference between the known reference system and the system of interest, we use the linear parametrization of the potential energy function

$$U(\lambda) = \lambda U_1 + (1-\lambda)U_0 \; .$$

From Eqn. 152 we know how to compute the derivative of the free energy with respect to $\lambda$ and hence we can express the free energy difference $F_1 - F_0$ as

$$F_1 - F_0 = \int_0^1 d\lambda \, \langle U_1 - U_0 \rangle_{NVT\lambda} \qquad (153)$$

This expression (first derived by Kirkwood), although useful for simulations, is not particularly useful for theoretical estimates of the free energy difference $F_1 - F_0$. However, we can make progress by considering

$$\left(\frac{\partial^2 F}{\partial \lambda^2}\right)_{NVT\lambda}$$

For the linear parametrization considered here, it is straightforward to show that

$$\left(\frac{\partial^2 F}{\partial \lambda^2}\right)_{NVT\lambda} = -\beta\left(\left\langle (U_1 - U_0)^2 \right\rangle_{NVT\lambda} - \langle (U_1 - U_0) \rangle^2_{NVT\lambda}\right) \qquad (154)$$

The important thing to note is that the second derivative of $F$ with respect to $\lambda$ is always negative (or zero). This implies that

$$\left(\frac{\partial F}{\partial \lambda}\right)_{NVT\lambda=0} \geq \left(\frac{\partial F}{\partial \lambda}\right)_{NVT\lambda}$$

and hence

$$F_1 \leq F_0 + \langle U_1 - U_0 \rangle_{NVT\lambda=0} \tag{155}$$

This variational principle for the free energy is known as the Gibbs-Bogoliubov inequality. It implies that we can compute an upper bound to the free energy of the system of interest, from knowledge of the average of $U_1 - U_0$ evaluated for the reference system. Of course, the usefulness of Eqn. 155 depends crucially on the quality of the choice of reference system. A good reference system is not necessarily one that is close in free energy to the system of interest, but one for which the fluctuations in de potential energy difference $U_1 - U_0$ are small. Thermodynamic perturbation theory for simple liquids has been very successful, precisely because the structure of the reference system (hard-sphere fluid) and the liquid under consideration (e.g. Lennard-Jones) is very similar. As a result, $< U_1 - U_0 >_\lambda$ hardly depends on $\lambda$ and, as a consequence, its derivative (Eqn. 154) is very small.

## 16.1 Perturbation theory for hard-core systems?

One drawback of the conventional formulation of thermodynamic perturbation theory is that it fails if the perturbation becomes very large, even when it is intuitively clear that the actual free energy difference between the reference system and the perturbed system should be small. Consider for instance a simple fluid with a steeply repulsive, but continuous potential. The free energy of this system will be very close to that of a hard-sphere reference system, provided that we make an optimal choice for the hard-sphere diameter $\sigma$ (see e.g. [49]). However, if we would try the inverse, i.e. compute the free energy of the hard-sphere fluid, starting from the continuous reference system, then Eqn. 155 would always predict an infinite free energy for the hard-sphere fluid. Admittedly, this example is not very realistic. But there are many cases where one *would* like to use a reference system with continuous interactions to model a system with hard-core interaction: for instance, one might wish to use an Einstein crystal as a reference system for a hard-sphere crystal, or one might be interested in developing a mean-field (Maier-Saupe [88]) model for a liquid crystal consisting of hard rods or platelets. To my knowledge, this problem seems to bother other people less than it bothers me. In fact, I have never seen the simple derivation that I present below in the literature. But I guess that it must exist somewhere.

Consider the case that we wish to estimate the Helmholtz free energy $F_h$ of a model system characterized by a potential energy function $U_h$. The subscript $h$ stands for “hard core”, because later, I will consider the case the $U_h$ is a hard-core potential. At this stage, however, I make no assumptions about $U_h$. In addition, we have a simple reference system with a potential energy function $U_r$ (the $r$ stands reference. $U_r$ may be a continuous function, but again, that is not essential at this stage). In what follows, I denote the configurational part of the partition functions of the two systems by $Z_h$ and $Z_r$ respectively. We assume that the free energy of the reference system ($F_r$) is known. Now consider two related model systems, one with a potential energy function $U_h/2$ and the other with potential energy $U_r/2$. We construct the following non-negative expression

$$g(\lambda) \equiv (\exp(-\beta U_h/2) + \lambda \exp(-\beta U_r/2))^2$$

where $\lambda$ is an arbitrary real number. Let us now consider the integral of $g(\lambda)$ over all configuration space.

$$\begin{aligned} \int d\mathbf{r}^N g(\lambda) &= \int d\mathbf{r}^N \exp(-\beta U_h) + 2\lambda \int d\mathbf{r}^N \exp(-\beta(U_h + U_r)/2) + \int d\mathbf{r}^N \exp(-\beta U_r) \\ &= Z_h + 2\lambda Z_{hr} + \lambda^2 Z_r \ , \end{aligned} \tag{156}$$

where $Z_{hr}$ is defined as

$$Z_{hr} \equiv \int d\mathbf{r}^N \exp(-\beta(U_h + U_r)/2)$$

As $g(\lambda)$ is non-negative, it follows that the expression in the last line of Eqn. 156 must also be non-negative. But Eqn. 156 is a simple quadratic equation in $\lambda$. Hence, we can immediately conclude that

$$Z_r Z_h \geq Z_{hr}^2 \tag{157}$$

We can rewrite this in the form of a simple variational expression for $Z_h$:

$$Z_h \geq \left(\frac{Z_{hr}}{Z_r}\right)^2 Z_r \tag{158}$$

or,

$$F_h \leq F_r - 2k_B T \ln\left(\frac{Z_{hr}}{Z_r}\right) \tag{159}$$

Now let us consider two applications. First, the (conventional one) where the reference potential $U_r$ describes a hard-core interaction, while $U_h$ is continuous. Then we immediately get,

$$F_h \leq F_r - 2k_B T \ln \langle \exp(-\beta U_h/2) \rangle_r \ . \tag{160}$$

And, in the limit of weak perturbations (or, more generally, in the case that the fluctuations of $U_h$ in the reference system are negligible), we recover the old result

$$F_h \leq F_r + \langle U_h \rangle_r \ . \tag{161}$$

Now consider the more interesting limit, where $U_h$ is a hard-core potential and $U_r$ is a continuous reference potential. In that case, we can write Eqn. 159 as

$$F_h \leq F_r - 2k_B T \ln \langle \exp(-\beta(U_h - U_r/2)) \rangle_r \ . \tag{162}$$

# 17 Mean-field theory

The Gibbs-Bogoliubov inequality can be used as a starting point to derive mean-field theory, which can be considered as a systematic approximation for the free energy of a many-body system. For the sake of simplicity, we consider a many-body Hamiltonian of interacting spins

$$U_1 = -\frac{J}{2}\sum_{i=1}^{N}\sum_{jnni} s_i s_j \ .$$

We wish to approximate this model system, using a reference system with a much simpler Hamiltonian, namely one that consists of a sum of one-particle contributions, e.g.

$$U_0 = \sum_{i=1}^{N} h s_i$$

where $h$ denotes the effective "field" that replaces the interaction with the other particles. The free energy per particle of the reference system is given by

$$f_0(h) = -k_B T \ln \int d\mathbf{s} \exp(-\beta h s)$$

We can easily compute the average value of $s$ in the reference system

$$< s >_0 = \frac{\partial f_0(h)}{\partial h} \tag{163}$$

Now, we consider the Gibbs-Bogoliubov inequality (Eqn. 155)

$$\begin{aligned} f_1 &\leq f_0 + < u_1 - u_0 >_0 \\ &= f_0 + < -\frac{J}{2}\sum_{jnni} s_i s_j - h s_i >_0 \\ &= f_0 - \frac{J}{2} z < s >^2 - h < s > \end{aligned} \tag{164}$$

where, in the last line, we have introduced $z$, the coordination number of particle $i$. Moreover, we have used the fact that, in the reference system, different spins are uncorrelated. We now look for the optimum value of $h$, i.e. the one that minimizes our estimate of $f_1$. Carrying out the differentiation with respect to $h$, we find

$$\begin{aligned} 0 &= \frac{\partial f_0 - \frac{J}{2} z < s >^2 - h < s >}{\partial h} \\ &= < s > - (Jz < s > + h)\frac{\partial < s >}{\partial h} - < s > \\ &= -(Jz < s > + h)\frac{\partial < s >}{\partial h} \end{aligned} \tag{165}$$

And hence,

$$h = -Jz < s > \tag{166}$$

If we insert this expression for $h$ in Eqn. 163, we obtain an implicit equation for $< s >$, that can be solved to yield $< s >$ as a function of $T$. The free energy estimate that we obtain when inserting this value of $< s >$ in Eqn. 164 is

$$f_{MF} = f_0 + \frac{J}{2} z < s >^2 \tag{167}$$

The subscript $MF$ in this expression stands for the "mean-field" approximation. It is very important to note that the free energy that results from the mean-field approximation is *not* simply the free energy of the reference system with the effective field. Many books on statistical mechanics are extremely vague (if not outright wrong) on this matter. A notable exception is the book by Yeomans [89].

The example of mean-field theory that I discussed above was chosen for its simplicity. However, the same variational method can be used to derive more general mean-field theories. Of course, the mean-field "recipe" described here cannot be used to approximate the free energy of hard-core models (for the same reason that conventional perturbation theory will not work in such cases). However, in that case, Eqn. 162 could be used as a starting point to devise a mean-field theory for systems with hard-core interactions.

# 18 Onsager's regression hypothesis

Diffusion is the process whereby an initially non-uniform concentration profile (*e.g.* an ink drop in water) is smoothened in the absence of flow (no stirring). Diffusion is caused by the molecular motion of the particles in the fluid. The macroscopic law that describes diffusion is known as Fick's law: it states that the flux $\mathbf{j}$ of the diffusing species is proportional to (minus) the gradient in the concentration of that species:

$$\mathbf{j} = -D\nabla c \tag{168}$$

where $D$, the constant of proportionality, is referred to as the diffusion coefficient. In what follows, I shall be discussing a particularly simple form of diffusion, namely the case that the molecules of the diffusing species are identical to the other molecules, but for a 'label' that does not affect the interaction of the labeled molecules with the others. For instance, this 'label' could be a particular polarization of the nuclear spin of the diffusing species or a modified isotopic composition. Diffusion of a labeled species among otherwise identical solvent molecules is called *self-diffusion.*

Let us now compute the concentration profile of the tagged species, under the assumption that a time $t = 0$, the tagged species was concentrated at the origin of our coordinate frame. In order to compute the time-evolution of the concentration profile, we must combine Fick's law with an equation that expresses conservation of the total amount of labeled material:

$$\frac{\partial c(r,t)}{\partial t} + \nabla \cdot \mathbf{j}(r,t) = 0 \tag{169}$$

Combining Eqn. 169 with Eqn. 168, we obtain

$$\frac{\partial c(r,t)}{\partial t} - D\nabla^2 c(r,t) = 0 \tag{170}$$

We can solve Eqn. 170 with the boundary condition

$$c(r,0) = \delta(r) \tag{171}$$

to yield

$$c(r,t) = \frac{1}{(4\pi Dt)^{d/2}} \exp(-\frac{r^2}{4Dt}) \ . \tag{172}$$

As before, $d$ denotes the dimensionality of the system. In fact, for what follows we do not need $c(r,t)$ itself, but just the time-dependence of its second moment

$$< r^2(t) > \equiv \int d\mathbf{r}\ c(r,t) r^2 \ , \tag{173}$$

where we have used the fact that we have imposed

$$\int d\mathbf{r}\ c(r,t) = 1 \ . \tag{174}$$

We can directly obtain an equation for the time-evolution of $< r^2(t) >$ by multiplying Eqn. 170 by $r^2$ and integrating over all space. This yields

$$\frac{\partial}{\partial t} \int d\mathbf{r}\ r^2 c(r,t) = D \int d\mathbf{r}\ r^2 \nabla^2 c(r,t) \tag{175}$$

The left hand side of this equation is simply equal to

$$\frac{\partial < r^2(t) >}{\partial t} \tag{176}$$

Applying partial integration to the right-hand side, we obtain

$$\begin{aligned}
\frac{\partial < r^2(t) >}{\partial t} &= D \int d\mathbf{r}\ r^2 \nabla^2 c(r,t) \\
&= D \int d\mathbf{r}\ \nabla (r^2 \nabla c(r,t)) - D \int d\mathbf{r}\ (\nabla r^2) \cdot (\nabla c(r,t)) \\
&= D \int d\mathbf{S}\ (r^2 \nabla c(r,t)) - 2D \int d\mathbf{r}\ (\mathbf{r}) \cdot (\nabla c(r,t)) \\
&= 0 - 2D \int d\mathbf{r}\ (\nabla \cdot \mathbf{r} c(r,t)) + 2D \int d\mathbf{r}\ (\nabla \cdot \mathbf{r}) c(r,t) \\
&= 0 + 2dD \int d\mathbf{r}\ c(r,t) \\
&= 2dD
\end{aligned} \tag{177}$$

Eqn. 177 relates the diffusion coefficient $D$ to the width of the concentration profile. This relation was first derived by Einstein. It should be realized that, whereas $D$ is a macroscopic transport coefficient, $< r^2(t) >$ has a *microscopic* interpretation: it is the mean-square distance over which the labeled molecules have moved in a time-interval $t$. This immediately suggests how to 'measure' $D$ in a computer simulation: for every particle $i$, we measure the distance traveled in time $t$, $\Delta\mathbf{r}_i(t)$ and we plot the mean square of these distances as a function of the time $t$:

$$< (\Delta r(t))^2 >= \frac{1}{N}\sum_{i=1}^{N}(\Delta\mathbf{r}_i(t))^2 \tag{178}$$

The displacement $\Delta\mathbf{r}(t)$ that we are interested in is simply the time-integral of the velocity of the tagged particle:

$$\Delta\mathbf{r}(t) = \int_0^t \mathbf{v}(t')\ dt'\ . \tag{179}$$

Eqn. 179 allows us to express the diffusion coefficient directly in terms of the particle velocities. We start with the relation

$$2D = \lim_{t\to\infty}\frac{\partial < x^2(t) >}{\partial t} \tag{180}$$

where, for convenience, we consider only one Cartesian component of the mean-square displacement. If we write $x(t)$ as the time-integral of the $x$-component of the tagged-particle velocity, we get

$$\begin{aligned} < x^2(t) > &= < (\int_0^t dt'\ v_x(t'))^2 > \\ &= \int_0^t\int_0^t dt'dt'' < v_x(t')v_x(t'') > \\ &= 2\int_0^t\int_0^{t'} dt'dt'' < v_x(t')v_x(t'') > \end{aligned} \tag{181}$$

The quantity $< v_x(t')v_x(t'') >$ is called the *velocity auto-correlation function.* It measures the correlation between the velocity of a particle at times $t'$ and $t''$. The velocity auto-correlation function (VACF) is an *equilibrium* property of the system, because it describes correlations between velocities at different times along an equilibrium trajectory. As equilibrium properties are invariant under a change of the time-origin, the VACF depends only on the *difference* of $t'$ and $t''$. Hence,

$$< v_x(t')v_x(t'') >=< v_x(t'-t'')v_x(0) > \tag{182}$$

Inserting Eqn. 181 in Eqn. 180, we obtain

$$\begin{aligned} 2D &= \lim_{t\to\infty} 2\int_0^t dt'' < v_x(t-t'')v_x(0) > \\ D &= \int_0^\infty d\tau\ < v_x(\tau)v_x(0) >\ . \end{aligned} \tag{183}$$

In the last line of Eqn. 183 we introduced the coordinate $\tau \equiv t - t''$. Hence, we see that we can relate the diffusion coefficient $D$ to the integral of the velocity auto-correlation function. Such a relation between a transport coefficient and an integral over a time-correlation function is called a 'Green-Kubo' relation. Green-Kubo relations have been derived for many other transport coefficients, such as the shear viscosity $\eta$,

$$\eta = \frac{1}{Vk_BT}\int_0^\infty dt \ < \sigma^{xy}(0)\sigma^{xy}(t) > \tag{184}$$

with

$$\sigma^{xy} = \sum_{i=1}^{N}\left( m_i v_i^x v_i^y + \frac{1}{2}\sum_{j\neq i} x_{ij} f_y(r_{ij})\right) \tag{185}$$

the thermal conductivity $\lambda$:

$$\lambda = \frac{1}{Vk_BT^2}\int_0^\infty dt \ < j_z^e(0) j_z^e(t) > \tag{186}$$

with

$$j_z^e = \frac{d}{dt}\sum_{i=1}^{N} z_i \frac{1}{2}\left( m_i v_i^2 + \sum_{j\neq i} v(r_{ij})\right) \tag{187}$$

and electrical conductivity $\sigma$

$$\sigma = \frac{1}{Vk_BT}\int_0^\infty dt \ < J_x^{el}(0) J_x^{el}(t) > \tag{188}$$

with

$$J_x^{el} = \sum_{i=1}^{N} q_i v_i^x \tag{189}$$

For details, see *e.g.* ref. [49]. Time correlation functions can easily be measured in a Molecular Dynamics simulation. It should be emphasized that for classical systems, the Green-Kubo relation for $D$ and the Einstein relation are strictly equivalent. There may be practical reasons to prefer one approach over the other, but the distinction is never fundamental. In the next section, we shall discuss time-correlation functions from a statistical-mechanical point of view.

# 19 Linear Response Theory

The Green-Kubo relations presented in the previous section are but an example of the relation that exists between transport phenomena and time-correlation functions. In fact, Onsager was the first to suggest that a disturbance created in a system by a weak external perturbation decays in the same way as a spontaneous fluctuation in equilibrium. The statistical mechanical theory that provides this link between correlation functions and response to weak perturbations is called *linear response theory.* I shall give a very simple introduction to linear response theory, mainly to illustrate the "mechanical" basis of Onsager's regression hypothesis. For a more detailed discussion, the reader is referred to any modern textbook on statistical mechanics *e.g.*, ref. [8]. A simple introduction (very similar to the one presented here) is given in the book by Chandler [90], while an extensive discussion of linear-response theory in the context of the theory of liquids is given in [49].

## 19.1 Static response

First, we consider the static response of a system to a weak applied field. The field could, for instance be an electric field, and the response might be the electric polarization. Suppose that we are interested in the response of a property that can be expressed as the ensemble average of a dynamical variable $A$. In the presence of an external perturbation, the average of $A$ changes from its equilibrium value $< A >_0$ to $< A >_0 + < \Delta A >$. Next, we must specify the perturbation. We assume that the perturbation can also be written as an explicit function of the coordinates (and, possibly, momenta) of the particles in the system. The effect of the perturbation is to change the Hamiltonian $H_0$ of the system, to $H_0$ - $\lambda B(\mathbf{p}^N, \mathbf{q}^N)$. For instance, in the case of an electric field along the $x$-direction, the change in $H$ would be $\Delta H = -E_x M_x(\mathbf{q}^N)$, where $M_x$ is the $x$-component of the total dipole moment of the system. The electric field $E_x$ corresponds to the parameter $\lambda$. We can immediately write down the general expression for $< \Delta A >$

$$< A >_0 + < \Delta A > = \frac{\int \mathrm{d},\ \ \exp[-\beta(H_0 - \lambda B)]A}{\int \mathrm{d},\ \ \exp[-\beta(H_0 - \lambda B)]}$$

where we have used the symbol , to denote $\{\mathbf{p}^N, \mathbf{q}^N\}$, the phase-space coordinates of the system. Let us now compute the part of $< \Delta A >$ that varies linearly with $\lambda$. To this end, we compute

$$\left(\frac{\partial < \Delta A >}{\partial \lambda}\right)_{\lambda=0}$$

Straightforward differentiation shows that

$$\left(\frac{\partial < \Delta A >}{\partial \lambda}\right)_{\lambda=0} = \beta\{< AB >_0 - < A >_0 < B >_0\} \tag{190}$$

To take again the example of the electric polarization, let us compute the change in dipole moment of a system due to an applied field $E_x$:

$$< M_x > = E_x \left(\frac{\partial M_x}{\partial E_x}\right)_{E_x=0} = \beta E_x\{< M_x^2 > - < M_x >^2\}$$

Suppose that we wish to compute the electric susceptibility of an ideal gas of non-polarizable dipolar molecules with dipole moment $\mu$. In that case,

$$\begin{aligned}\{< M_x^2 > - < M_x >^2\} &= \sum_{i,j=1}^{N} < \mu_x^i \mu_x^j > \\ &= N < (\mu_x^i)^2 > \\ &= \frac{N\mu^2}{3}\end{aligned}$$

and hence,

$$P_x \equiv \frac{M_x}{V} = \frac{\mu^2 \rho}{3k_B T} E_x \ .$$

Of course, this example is special because it can be evaluated exactly. But, in general, we can only compute the expression (equation (190)) for the susceptibility, numerically. It should also be noted that the computation of the dielectric susceptibility is quite a bit more subtle than suggested in the above example (see *e.g.* the discussion in the book of Allen and Tildesley [12] and the article by McDonald in [91]).

## 19.2 Dynamic response

Thus far, we only considered the static response to a constant perturbation. Let us now consider a very simple time-dependent perturbation. We begin by preparing the system in the presence of a weak, constant perturbation ($\lambda B$). The static response of $A$ to this perturbation, is given by equation (190). At time $t$=0, we discontinuously switch off the external perturbation. The response $\Delta A$ will now decay to zero. We can write down an expression for the average of $\Delta A$ at time $t$ :

$$< \Delta A(t) > = \frac{\int \mathrm{d}, \ \ \exp[-\beta(H_0 - \lambda B)] A(t)}{\int \mathrm{d}, \ \ \exp[-\beta(H_0 - \lambda B)]}$$

where $A(t)$ is value of $A$ at time $t$ if the system started at point , in phase space, and then evolved according to the natural time evolution of the em unperturbed system. For convenience, we have assumed that the average of $A$ in the unperturbed system vanishes. In the limit $\lambda \to 0$, we can write

$$\begin{aligned}< \Delta A(t) > &= \beta\lambda \frac{\int \mathrm{d}, \ \ \exp[-\beta H_0] B A(t)}{\int \mathrm{d}, \ \ \exp[-\beta H_0]} \\ &= \beta\lambda < B(0) A(t) > \qquad (191)\end{aligned}$$

To give a specific example, consider once again a gas of dipolar molecules in the presence of a weak electric field $E_x$. The perturbation is equal to $-E_x M_x$. At time $t$=0, we switch off the electric field. When the field was still on, the system had a net dipole moment. When the field is switched off, this dipole moment decays:

$$< M_x(t) >= E_x\beta < M_x(0)M_x(t) >$$

In words, the decay of the macroscopic dipole moment of the system is determined by the dipole correlation function, which describes the decay of spontaneous fluctuations of the dipole moment in equilibrium. This relation between the decay of the response to an external perturbation and the decay of fluctuations in equilibrium is an example of Onsager's regression hypothesis.

It might seem that the above example of a constant perturbation that is suddenly switched off, is of little practical use, because we are interested in the effect of an arbitrary time-dependent perturbation. Fortunately, in the linear regime that we are considering, the relation given by equation (191) is enough to derive the general response.

To see this, let us consider a time-dependent external field $f(t)$ that couples to a mechanical property $B$, *i.e.*,

$$H(t) = H_0 - f(t)B\ .$$

To linear order in $f(t)$, the most general form of the response of a mechanical property $A$ to this perturbation is

$$< \Delta A(t) >= \int_{-\infty}^{\infty} \mathrm{d}t' \chi_{AB}(t,t')f(t') \tag{192}$$

where $\chi_{AB}$, the 'after-effect' function, describes the linear response. We know several things about the response of the system that allow us to simplify equation (192). First of all, the response must be *causal*, *i.e.*, there can be no response *before* the perturbation is applied. As a consequence,

$$\chi_{AB}(t,t') = 0 \text{ for } t < t'.$$

Secondly, the response at time $t$ to a perturbation at time $t'$ depends only on the time *difference* $t - t'$. Hence,

$$< \Delta A(t) >= \int_{-\infty}^{t} \mathrm{d}t' \chi_{AB}(t-t')f(t') \tag{193}$$

Note that, once we know $\chi$, we can compute the linear response of the system to an arbitrary time-dependent perturbating field $f(t')$. To find an expression for $\chi_{AB}$, let us consider the situation described above equation (191), namely an external perturbation that has a constant value $\lambda$ until $t = 0$ and zero from then on. From equation (193) it follows that the response to such a perturbation is

$$\begin{aligned} < \Delta A(t) > &= \lambda \int_{-\infty}^{0} \mathrm{d}t' \chi_{AB}(t-t') \\ &= \lambda \int_{t}^{\infty} \mathrm{d}\tau\ \chi_{AB}(\tau) \end{aligned} \tag{194}$$

If we compare this expression with the result of equation (191), we see immediately that

$$\int_t^\infty \mathrm{d}\tau \; \chi_{AB}(\tau) = \beta\lambda < B(0)A(t) >$$

or

$$\begin{aligned} \chi_{AB}(t) &= -\beta < B(0)\dot{A}(t) > \text{ for } t > 0. \\ &= 0 \text{ for } t \le 0. \end{aligned} \tag{195}$$

To give a specific example, consider the mobility of a molecule in an external field $F_x$. The Hamiltonian in the presence of this field is

$$H = H_0 - F_x x \; .$$

The phenomenological expression for the steady-state velocity of a molecule in an external field is

$$< v_x(t) >= \mu F_x \tag{196}$$

If we derive this relation in terms of correlation functions, we shall find a microscopic expression for the mobility $\mu$. From equation (193) through 195, we have

$$\begin{aligned} < v_x(t) > &= F_x \int_{-\infty}^{t} \mathrm{d}t' \chi_{v_x x}(t - t') \\ &= F_x \int_0^\infty \mathrm{d}\tau \chi_{v_x x}(\tau) \\ &= -\beta F_x \int_0^\infty \mathrm{d}\tau < x(0)\dot{v}_x(\tau) > \\ &= +\beta F_x \int_0^\infty \mathrm{d}\tau < v_x(0)v_x(\tau) > \end{aligned} \tag{197}$$

In the last line of equation (197), we have made use of the stationarity property of time-correlation functions

$$\frac{d}{dt} < A(t)B(t + t') >= 0$$

Carrying out the differentiation, we find

$$< \dot{A}(t)B(t + t') >= - < A(t)\dot{B}(t + t') > \; .$$

Combining equation (196) and equation (197), we find

$$\mu = \beta \int_0^\infty \mathrm{d}t < v_x(0)v_x(t) > \tag{198}$$

If we compare the above result with the Green-Kubo relation for the self-diffusion coefficient (equation (183)) we recover the Einstein relation, $\mu = \beta D$.

## 19.3 Dissipation

Many experimental techniques probe the dynamics of a many-body system by measuring the absorption of some externally applied field (*e.g.*, visible light, infrared radiation, microwave radiation). Linear-response theory allows us to establish a simple relation between the absorption spectrum and the Fourier transform of a time-correlation function. To see this, let us again consider an external field that is coupled to a dynamical variable $A(\mathbf{p}^N, \mathbf{q}^N)$. The time-dependent Hamiltonian of the system is:

$$H(t) = H_0 - f(t)A(\mathbf{p}^N, \mathbf{q}^N) \; .$$

Note that the only quantity that is explicitly time-dependent is $f(t)$. As the Hamiltonian depends on time, the total energy $E$ of the system also changes with time.

$$E(t) =< H(t) >$$

Let us compute the average rate of change of the energy of the system. This is the amount of energy that is absorbed (or emitted) by the system, per unit time.

$$\begin{aligned} \frac{\partial E}{\partial t} &= \left\langle \frac{\mathrm{d}H}{\mathrm{d}t} \right\rangle \qquad (199) \\ &= \left\langle \sum_i \left( \dot{\mathbf{q}}_i \frac{\partial H}{\partial \mathbf{q}_i} + \dot{\mathbf{p}}_i \frac{\partial H}{\partial \mathbf{p}_i} \right) + \frac{\partial H}{\partial t} \right\rangle \end{aligned}$$

But, from Hamilton's equations of motion we have

$$\dot{\mathbf{q}}_i = \frac{\partial H}{\partial \mathbf{p}_i}$$

and

$$\dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{q}_i}$$

As a consequence, equation (199) simplifies to

$$\begin{aligned} \frac{\partial E}{\partial t} &= \left\langle \frac{\partial H}{\partial t} \right\rangle \\ &= -\left\langle \dot{f}(t) A(\mathbf{p}^N, \mathbf{q}^N) \right\rangle \\ &= -\dot{f}(t) < A(t) > \qquad (200) \end{aligned}$$

One should note, however, that $< A(t) >$ itself is the response to the applied field $f$

$$< A(t) >= \int_{-\infty}^{\infty} \mathrm{d}t' \; \chi_{AA}(t - t') f(t')$$

Let us now consider the situation where $f(t)$ is a periodic field with frequency $\omega$ (*e.g.*, monochromatic light). In that case, we can write $f(t)$ as

$$f(t) = \mathrm{Re} f_\omega e^{\mathrm{i}\omega t}$$

and

$$\dot{f}(t) = \frac{\mathrm{i}\omega}{2}(f_\omega \mathrm{e}^{\mathrm{i}\omega t} - f_\omega^* \mathrm{e}^{-\mathrm{i}\omega t})$$

The average rate of energy dissipation is:

$$\begin{aligned} \frac{\partial E}{\partial t} &= -\dot{f}(t) < A(t) > \\ &= -\dot{f}(t) \int_{-\infty}^{\infty} \mathrm{d}t' \; \chi_{AA}(t-t') f(t') \end{aligned} \tag{201}$$

For a periodic field, we have

$$\begin{aligned} \int_{-\infty}^{\infty} \mathrm{d}t' \; \chi_{AA}(t-t') f(t') &= \frac{f_\omega \mathrm{e}^{\mathrm{i}\omega t}}{2} \int_{-\infty}^{\infty} \mathrm{d}t' \; \chi_{AA}(t-t') \mathrm{e}^{\mathrm{i}\omega(t'-t)} \\ &+ \frac{f_\omega^* \mathrm{e}^{-\mathrm{i}\omega t}}{2} \int_{-\infty}^{\infty} \mathrm{d}t' \; \chi_{AA}(t-t') \mathrm{e}^{-\mathrm{i}\omega(t'-t)} \\ &= \pi \left( f_\omega \mathrm{e}^{\mathrm{i}\omega t} \chi_{AA}(\omega) + f_\omega^* \mathrm{e}^{-\mathrm{i}\omega t} \chi_{AA}(-\omega) \right) \end{aligned} \tag{202}$$

where

$$\chi_{AA}(\omega) \equiv \frac{1}{2\pi} \int_0^{\infty} \mathrm{d}t \chi_{AA}(t) \mathrm{e}^{-\mathrm{i}\omega t} \; .$$

To compute $\dot{E}$, the rate of change of the energy, we must average

$$< \frac{\partial H}{\partial t} >$$

over one period $T$ $(= 2\pi/\omega)$, of the field:

$$\begin{aligned} \dot{E} &= \frac{-\pi}{2T} \int_0^T \mathrm{d}t \; \Big\{ \mathrm{i}\omega (f_\omega \mathrm{e}^{\mathrm{i}\omega t} - f_\omega^* \mathrm{e}^{-\mathrm{i}\omega t}) \\ &\times \; \Big[ f_\omega \mathrm{e}^{\mathrm{i}\omega t} \chi_{AA}(\omega) + f_\omega^* \mathrm{e}^{-\mathrm{i}\omega t} \chi_{AA}(-\omega) \Big] \Big\} \\ &= -\pi\omega |f_\omega|^2 \frac{\chi_{AA}(\omega) - \chi_{AA}(-\omega)}{2i} \\ &= -\pi\omega |f_\omega|^2 \mathrm{Im} \chi_{AA}(\omega) \end{aligned} \tag{203}$$

We use the relation between $\chi_{AA}(t)$ and the auto-correlation function of $A$ (Eqn. 195)

$$\chi_{AA}(\omega) = \frac{1}{2\pi} \int_0^{\infty} \mathrm{d}t \; \mathrm{e}^{-\mathrm{i}\omega t} (-\beta < A(0) \dot{A}(t) >)$$

The imaginary part of $\chi_{AA}(\omega)$ is given by

$$\begin{aligned}\mathrm{Im}\chi_{AA}(\omega) &= \frac{\beta}{2\pi}\int_0^\infty \mathrm{d}t\ \sin(\omega t) < A(0)\dot{A}(t) > \\ &= \frac{-\beta}{4\pi}\int_{-\infty}^\infty \mathrm{d}t\, \omega\cos(\omega t) < A(0)A(t) > \end{aligned} \tag{204}$$

Finally, we obtain

$$\dot{E} \;=\; |f_\omega|^2\frac{\beta\omega^2}{4}\int_{-\infty}^\infty \mathrm{d}t\ \cos(\omega t) < A(0)A(t) > \tag{205}$$

Hence, from knowledge of the autocorrelation function of the quantity that couples with the applied field, we can compute the shape of the absorption spectrum. The above relation was derived assuming classical dynamics and is therefore only valid if $\hbar\omega \ll k_B T$. However, it is also possible to derive a quantum-mechanical version of linear-response theory that is valid for arbitrary frequencies (see *e.g.*, ref. [8]).

To give a specific example, let us compute the shape of the absorption spectrum of a dilute gas of polar molecules. In that case, the relevant correlation function is the dipole auto-correlation function

$$< M_x(0)M_x(t) >= \frac{N}{3} < \mu(0)\cdot\mu(t) > \ .$$

For molecules that rotate almost freely (*almost*, because otherwise there would be no dissipation), $\mu(0)\cdot\mu(t)$ depends on time because each molecule rotates. For a molecule with a rotation frequence $\omega$, we have

$$\mu(0)\cdot\mu(t) = \mu^2\cos(\omega t)$$

and for an assembly of molecules with a thermal distribution of rotational velocities $P(\omega)$, we have

$$< \mu(0)\cdot\mu(t) >= \mu^2\int \mathrm{d}\omega P(\omega)\cos(\omega t)$$

The rate of absorption of radiation is then given by

$$\dot{E} = \frac{\pi\beta\omega^2 N\mu^2}{12}P(\omega)|f(_\omega|^2) \tag{206}$$

For more details about the relation between spectroscopic properties and time-correlation functions, the reader is referred to the article by Madden in ref. [91].

In the above derivation of linear response theory, we have assumed that the system we prepare the system in an equilibrium state with the perturbation *on* and then allow the system to relax to a new equilibrium state with the perturbation *off*. However, this will not always work. Consider, for instance, electrical conductivity. In that case, the perturbation is an electrical field that will cause a current to flow in the system. Hence, the state in which we prepared the system with the field on is *not* an equilibrium state, but a steady *non-equilibrium* state. The same holds, for instance, for a system under steady shear. It would seem that, under such circumstances, one cannot use the framework of linear response theory in its simplest form to derive transport coefficients such as the electrical conductivity $\sigma$ or the viscosity $\eta$.

### 19.3.1 Electrical conductivity

Fortunately, things are not quite as bad as that. Consider, for example, electrical conductivity. Indeed, if we put a conducting system in an external field, we will generate a non-equilibrium steady state. However, what we *can* do is to perturb the system by switching on a weak, uniform *vector potential* **A**. The Hamiltonian of the system with the vector potential switched on is

$$H' = \sum_{i=1}^{N} \frac{1}{2m_i}(\mathbf{p}_i - \frac{e_i}{c}\mathbf{A})^2 + U_{pot}; . \tag{207}$$

The system described by this Hamiltonian satisfies the same equations of motion as the unperturbed system (**A** is a gauge field) and the system will be in an equilibrium state at $t = 0$. We then abruptly switch off the vector potential. From electrodynamics, we know that a time dependent vector potential generates an electric field:

$$\mathbf{E} = \frac{-1}{c}\dot{\mathbf{A}} . \tag{208}$$

In the present case, the electral field will be an infinitesimal $\delta$-spike at $t = 0$

$$\mathbf{E}(t) = \frac{1}{c}\mathbf{A}\delta(t) . \tag{209}$$

We can compute the current that results, in the standard way. We note that we can write $H'$ in Eqn. 207 as

$$\begin{aligned} H' &= H_0 - \sum_{i=1}^{N} \frac{e_i}{cm_i}\mathbf{p}_i \cdot \mathbf{A} + \mathcal{O}(A^2) \\ &= H_0 - \frac{\mathbf{A}}{c}\int d\mathbf{r} \sum_{i=1}^{N} \frac{e_i}{m_i}\mathbf{p}_i\delta(\mathbf{r}_i - \mathbf{r}) \\ &= H_0 - \frac{\mathbf{A}}{c}\int d\mathbf{r}\, \mathbf{j}(\mathbf{r}) \end{aligned} \tag{210}$$

where $\mathbf{j}(\mathbf{r})$ denotes the current density at point $\mathbf{r}$. The average current density at time $t$ due to the perturbation is given by

$$< \mathbf{j}(t) >= \frac{\mathbf{A}}{cVk_BT}\int d\mathbf{r}d\mathbf{r}' < \mathbf{j}(\mathbf{r},0)\mathbf{j}(\mathbf{r}',t) > \ . \tag{211}$$

The phenomenological expression for the current response to an applied $\delta$-function electric field spike is (see Eqn. 193)

$$\begin{aligned} < \mathbf{j}(t) > &= \int_{-\infty}^{t} \mathrm{d}t' \sigma(t-t') E(t') \\ &= \sigma(t) \frac{A}{c} \end{aligned} \tag{212}$$

From this it immediately follows that

$$\sigma(t) = \frac{1}{V k_B T} \int d\mathbf{r} d\mathbf{r}' < \mathbf{j}(\mathbf{r}, 0) \mathbf{j}(\mathbf{r}', t) > \ . \tag{213}$$

The DC conductivity is then given by

$$\sigma(\omega = 0) = \frac{1}{V k_B T} \int_0^\infty dt \int d\mathbf{r} d\mathbf{r}' < \mathbf{j}(\mathbf{r}, 0) \mathbf{j}(\mathbf{r}', t) > \ . \tag{214}$$

### 19.3.2 Viscosity

The corresponding linear response expression for the viscosity seems more subtle because shear is a usually not interpreted in terms of an external field acting on all molecules. Still, we can use, by analogy to the electrical conductivity cases, a canonical transformation, the time-derivative of which corresponds to uniform shear. To achieve this, we consider a system of $N$ particles with coordinates $\mathbf{r}^M$ and Hamiltonian

$$H_0 = \sum_{i=1}^{N} p_i^2/(2m_i) + U(\mathbf{r}^N) \ . \tag{215}$$

Now consider another system, described by a set of coordinates $\mathbf{r'}^N$ that is related to $\mathbf{r}^N$ by a linear transformation:

$$\mathbf{r'}_i = \mathbf{h} \cdot \mathbf{r}_i \ . \tag{216}$$

The Hamiltonian for the new system can be written as

$$H_1 = \sum_{i=1}^{N} \frac{1}{2m_i} \mathbf{p'}_i \cdot \mathbf{G}^{-1} \cdot \mathbf{p'}_i + U(\mathbf{r'}^N) \ , \tag{217}$$

where $\mathbf{G}$, the metric tensor is defined as

$$\mathbf{G} \equiv \mathbf{h}^T \cdot \mathbf{h} \tag{218}$$

We assume that $\mathbf{h}$ differs infinitesimally from the unit matrix $\mathbf{I}$:

$$\mathbf{h} = \mathbf{I} + \boldsymbol{\epsilon} \tag{219}$$

In the case that we are interested in the effect of uniform shear, we could for instance choose $\epsilon_{xy} = \epsilon$, while all other elements of $\epsilon_{\alpha\beta}$ are zero. Now consider the case that we equilibrate the system with Hamiltonian $H_1$ and, at time $t = 0$, we switch off the infinitesimal deformation $\epsilon$. This means that, at $t = 0$, the system experiences a $\delta$-function spike in the shear rate

$$\frac{\partial v_x}{\partial y} = -\epsilon\delta(t) \tag{220}$$

We can compute the time-dependent response of the shear stress, $\sigma_{xy}(t)$, to the sudden change from $H_1$ to $H_0$.

$$< \sigma_{xy}(t) >= -\epsilon\frac{1}{Vk_BT} < \sigma_{xy}(0)\sigma_{xy}(t) > \tag{221}$$

By combining Eqns. 220 and 221 with Eqn. 193, we immediately see that the steady-state stress that results from an steady shear is given by

$$\sigma_{xy} = \frac{\partial v_x}{\partial y} \times \frac{1}{Vk_BT}\int_0^\infty dt < \sigma_{xy}(0)\sigma_{xy}(t) > \tag{222}$$

and the resulting expression for the shear viscosity $\eta$ is

$$\eta = \frac{1}{Vk_BT}\int_0^\infty dt < \sigma_{xy}(0)\sigma_{xy}(t) > \ . \tag{223}$$

## 19.4 Rare Events

We conclude this section with a discussion of a special class of transport phenomena, namely activated processes. Activated processes require special attention because a naive application of linear-response theory will yield results that are essentially useless. As an example, we consider uni-molecular reaction $A \rightleftharpoons B$, in which species $A$ is transformed into species $B$. We limit our discussion to those cases where the rate-limiting step of the reaction can be described as a classical barrier-crossing problem. Of course, there are many chemical reactions that do not fit this description. On the other hand, there are many other activated processes (e.g. classical diffusion through a membrane) that do. Our discussion of activated processes is based on Chandler's approach [90].

Let us first look at the phenomenological description of uni-molecular reactions. We denote the number density of species $A$ and $B$ by $c_A$ and $c_B$, respectively. The phenomenological rate equations are

$$\begin{aligned} \frac{dc_A(t)}{dt} &= -k_{BA}c_A(t) + k_{AB}c_B(t) \\ \frac{dc_B(t)}{dt} &= +k_{BA}c_A(t) - k_{AB}c_B(t) \end{aligned} \tag{224}$$

Clearly, as the number of molecules is constant in this conversion reaction, the total number density is conserved.

$$\frac{d(c_A(t) + c_B(t))}{dt} = 0 \tag{225}$$

In equilibrium, all concentrations are time-independent, *i.e.*, $\dot{c}_A = \dot{c}_B = 0$. This implies that

$$K \equiv \frac{< c_A >}{< c_B >} = \frac{k_{BA}}{k_{AB}} \tag{226}$$

where $K$ is the equilibrium constant of the reaction. Let us now consider what happens if we take a system at equilibrium, and apply a small perturbation $\Delta c_A$, to the concentration of species $A$ (and thereby of species $B$). We can rewrite the rate equation that determine the decay of this perturbation as follows

$$\frac{d\Delta c_A(t)}{dt} = -k_{BA}\Delta c_A(t) - k_{AB}\Delta c_A(t) \tag{227}$$

where we have used Eqns. 225 and 226. The solution to this equation is

$$\Delta c_A(t) = \Delta c_A(0)e^{-(k_{BA}+k_{AB})t} \equiv \Delta c_A(0)e^{-t/\tau_R} \tag{228}$$

where we have defined the reaction time constant

$$\tau_R = (k_{AB} + k_{BA})^{-1} = k_{BA}^{-1}(1 + \frac{< c_A >}{< c_B >}) = \frac{c_B}{k_{BA}} \tag{229}$$

where we have assumed that the total concentration $c_A + c_B = 1$. With this normalization, $c_A$ is simply the probability that a given molecule is in 'state' $A$.

Thus far, we have discussed the reaction from a macroscopic, phenomenological point of view. Let us now look at the microscopics. We will do this in the framework of linear response theory. First of all, we must have a microscopic description of the reaction. This means that we need a recipe that allows us to measure how far the reaction has progressed. In the case of diffusion from one free energy minimum to another, over a barrier, we might use the fraction of the distance traveled as a 'reaction coordinate'. In general, reaction coordinates may be complicated, non-linear functions of the coordinates of all particles. It is convenient to think of the reaction coordinate $q$ simply as a generalized coordinate.

By analogy to the discussion in section 19, we will consider an external perturbation that changes the relative probabilities of finding species $A$ and $B$. To achieve this,we add to the Hamiltonian a term that *lowers* the potential energy for $q < q^*$, where $q^*$ denotes the value of the reaction coordinate at the top of the barrier.

$$H = H_0 - \epsilon\theta(q^* - q) \tag{230}$$

where $\theta(x)$ is the Heavyside step-function, $\theta(x) = 1$ for $x > 0$ and $\theta(x) = 0$ otherwise. $\epsilon$ is a parameter that measures the strength of the perturbation. As we are interested in the linear response, we shall consider the limit $\epsilon \to 0$. Let us first consider the effect of a static perturbation of this type on the probability to find a given molecule in state $A$. We note that

$$\Delta c_A =< c_A >_\epsilon - < c_A >_0 =< \theta_A >_\epsilon - < \theta_A >_0 \tag{231}$$

From Eqn. 190 of section 19.1, we find immediately that

$$\frac{\partial \Delta c_A}{\partial \epsilon} = \beta(< \theta_A^2 >_0 - < \theta_A >_0^2) \tag{232}$$

This equation can be simplified by noting that $\theta^2(x) = \theta(x)$, hence

$$\frac{\partial \Delta c_A}{\partial \epsilon} = \beta\{< \theta_A >_0 (1- < \theta_A >_0)\} = \beta < c_A >< c_B > \tag{233}$$

Now, we consider what happens if we suddenly switch off the perturbation at time $t = 0$. The concentration of $A$ will relax to its equilibrium value as described in Eqn. 191 and we find that, to first order in $\epsilon$

$$\begin{aligned} \delta c_A(t) &= \beta\epsilon \frac{\int d,\, e^{-\beta H_0}(\theta(0)- < \theta >)(\theta(t)- < \theta >)}{\int d,\, e^{-\beta H_0}} \\ &= \beta\epsilon < \Delta\theta(0)\Delta\theta(t) > \end{aligned} \tag{234}$$

Finally, we can use Eqn. 233 to eliminate $\epsilon$ from the above equation, and we find the following expression for the relaxation of an initial perturbation in the concentration of species $A$

$$\Delta c_A(t) = \Delta c_A(0) \frac{< \Delta\theta(0)\Delta\theta(t) >}{< c_A >< c_B >} \tag{235}$$

If we compare this with the phenomenological expression, Eqn. 228, we see that

$$e^{-t/\tau_R} = \frac{< \Delta\theta(0)\Delta\theta(t) >}{< c_A >< c_B >} \tag{236}$$

Actually, we should be cautious with this identification. For very short times (*i.e.*, typical time-scales for molecular motion), we should *not* expect the autocorrelation function of the concentration fluctuations to decay exponentially. Only at times that are long compared to typical molecular processes, should we expect Eqn. 236 to hold. Let us assume that we are in this regime. Then we can obtain a expression for $\tau_R$ by differentiating Eqn. 236:

$$-\tau_R^{-1} e^{-t/\tau_R} = \frac{< \theta(0)\dot{\theta}(t) >}{< c_A >< c_B >} = -\frac{< \dot{\theta}(0)\theta(t) >}{< c_A >< c_B >} \tag{237}$$

where we have dropped the $\Delta$'s, because the time-derivative of the equilibrium concentration vanishes. Hence, for times that are long compared to molecular times, but still very much shorter than $\tau_R$, we can write

$$\tau_R^{-1} = \frac{< \dot{\theta}(0)\theta(t) >}{< c_A >< c_B >} \tag{238}$$

or, if we recall Eqn. 229 for the relation between $k_{BA}$ and $\tau_R$, we find

$$k_{BA}(t) = \frac{< \dot{\theta}(0)\theta(t) >}{< c_A >} \tag{239}$$

In this equation, we have indicated the time-dependence of $k_{BA}(t)$ is indicated explicitly. However, we recall that it is only the long-time plateau value of $k_{AB}(t)$ that enters into the phenomenological rate equation. Finally, we can express the correlation function in Eqn. 239 by noting that

$$\dot{\theta}(q^* - q) = \dot{q}\frac{\partial\theta(q^* - q)}{\partial q} = -\dot{q}\delta(q^* - q) \tag{240}$$

Hence

$$\begin{aligned} k_{BA}(t) &= \frac{< \dot{q}\delta(q^* - q(0))\theta(q(t) - q^*) >}{< c_A >} \\ &= \frac{< \dot{q}\delta(q^* - q(0))\theta(q(t) - q^*) >}{< \theta(q^* - q) >} \end{aligned} \tag{241}$$

$< \theta(q^* - q) >$ denotes the probability to find the system somewhere in valley $A$ (the 'reactant' side, to use the language of chemical reactions). We can rephrase equation (241) in a form that makes the separation in statics and dynamics more obvious. We do this by multiplying and dividing and multiplying the right hand side of equation (241) by $< \delta(q^* - q) >$. We then obtain

$$k_{BA} = \lim_{t\to\infty} \frac{< \dot{q}(0)\delta(q^* - q(0))\theta(q(t) - q^*) >}{< \delta(q^* - q(0)) >} \times \frac{< \delta(q^* - q) >}{< \theta(q^* - q) >} \tag{242}$$

The second term on the right-hand side of equation (242), *i.e.*, $< \delta(q^* - q) >$ / $< \theta(q^* - q) >$ denotes the probability density to find the system at the top of the barrier, divided by the probability that the system is on the reactant side of the barrier. This ratio, is completely determined by the height of the free-energy barrier and can therefore be measured by umbrella sampling. For instance, van Duijneveldt and Frenkel [7] have used umbrella sampling to estimate the free-energy barrier for crystal nucleation.

The first term on the left hand side of equation (242) is a conditional average, namely the average of the product $\dot{q}(0)\theta(q(t) - q^*)$, given that $q(0) = q^*$. We can write this term as

$$\lim_{t\to\infty} < \dot{q}(0)\theta(q(t) - q^*) >_{q(0)=q^*} \tag{243}$$

This dynamic quantity can be computed by Molecular Dynamics. In practice, constraint MD will be used to compute this average, in which the system is prepared under the initial constraint $q(0) = q^*$ and then released. It should be noted that the use of a constraint in the MD sampling does have a (slight) effect on the average in equation (243) [92]. The final result is that we have expressed the rate constant $k_{BA}$ exclusively in microscopic quantities that can be measured in a simulation [93, 90].

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# References

[1] M.N.Rosenbluth and A.W.Rosenbluth, J.Chem. Phys. **23**:356(1955)

[2] R.H. Swendsen and J.-S. Wang. *Phys. Rev. Lett.*, 58:86–88, 1987.

[3] K. Binder. *The Monte Carlo Method in Condensed Matter Physics*. Springer, Berlin, 1992.

[4] D. Wu, D. Chandler, and B. Smit. *J. Phys. Chem.*, 96:4077–4083, 1992.

[5]

[6] J. L. Lebowitz, J. K. Percus, and L. Verlet, Phys. Rev. **153**, 250 (1967).

[7] J. S. van Duijneveldt and D. Frenkel, J.Chem.Phys. **96**, 4655 (1992).

[8] L.E. Reichl, *A modern course in Statistical Physics* (University of Texas Press, Austin, 1980).

[9] H. Goldstein, *Classical Mechanics*, 2nd ed. (Addison-Wesley, Reading, 1980).

[10] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.N. Teller, and E. Teller. Equation of state calculations by fast computing machines. *J. Chem. Phys.*, 21:1087–1092, 1953.

[11] N.G. Van Kampen. *Stochastic Processes in Physics and Chemistry.* North-Holland, Amsterdam, 1981.

[12] M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).

[13] W.H. Press, B.P. Flannery, S.A. Teukolsky, and W.T. Vetterling. *Numerical Recipes: The art of scientific computing.* Cambridge University Press, Cambridge, 1986.

[14] M.H. Kalos and P.A. Whitlock. *Monte Carlo Methods.* John Wiley, New York, 1986.

[15] W.W. Wood and F.R. Parker. Monte Carlo equation of state of molecular interactions with Lennard-Jones potential. I. A supercritical isotherm at about twice the critical temperature. *J. Chem. Phys.*, 27:720–733, 1957.

[16] M.J. Mandel. On the properties of a periodic fluid. *J. Stat. Phys.*, 15:299–305, 1976.

W. W. Wood, J. Chem. Phys. **48**:415 (1968).

[17] I. R. McDonald, Mol. Phys. **23**:41 (1972).

[18] R. Eppenga and D. Frenkel, Mol. Phys. **52**:1303 (1984).

[19] A. Z. Panagiotopoulos, Mol. Phys. **61**:813 (1987).

[20] B. Smit, Ph. de Smedt, and D. Frenkel. *Mol. Phys.*, 68:931–950, 1989.

[21] A. Z. Panagiotopoulos, N. Quirke, M. Stapleton and D. J. Tildesley, Mol. Phys. **63**:527 (1988).

[22] A. Z. Panagiotopoulos, Mol. Phys. **62**:701 (1987).

[23] D.A. Kofke, *Mol. Phys.*, 78:1331–1336, 1993.

[24] D.A. Kofke, *J. Chem. Phys.*, 98:4149–4162, 1993.

[25] R. Agrawal and D.A. Kofke, *Mol. Phys.*, 85:43–59, 1995.

[26] R. Agrawal and D.A. Kofke, *Phys. Rev. Lett.*, 74:122–125, 1995.

[27] M. Dijkstra and D. Frenkel, Phys. Rev. E. **51**:5891–5898(1995)

[28] E.J. Meijer and F. El Azhar
J. Chem. Phys. **106**, 4678–4683 (1997).

[29] F.A. Escobedo and J.J. de Pablo, J. Chem. Phys. **106**:2911–2923(1997).

[30] B. Widom, J. Chem. Phys. **39**:2808 (1963).

[31] T. Garel and H. Orland, *J. Phys. A: Math. Gen.*, 23:L621–L626, 1990.

[32] P. Grassberger. *J. Phys. A: Math. Gen.*, 26:1023–1036, 1993.

[33] P. Grassberger. *J. Phys. A: Math. Gen.*, 26:2769–2776, 1993.

[34] P. Grassberger and R. Hegger. *J. Phys.: Condens. Matter*, 7:3089–3097, 1995.

[35] D. Frenkel, in M. Baus *et al.*, editor, *Observation, prediction and simulation of phase transitions in complex fluids*, pages 357–419, Dordrecht, 1995. NATO ASI, Kluwer.

[36] D.Frenkel, J.Phys. Condensed Matter **2(SA)**:265(1990)

[37] E.J.Meijer and D.Frenkel, Phys. Rev. Lett. **67**:1110(1991).

[38] G.C.A.M. Mooij and D. Frenkel, Mol. Phys. **74**:41(1991)

[39] G. M. Torrie and J. P. Valleau, J. Comp. Phys. **23**:187 (1977)

[40] G.D. Quinlan and S. Tremaine. On the reliability of gravitational n-body integrations. *Mon. Not. R. Astron. Soc.*, 259:505–518, 1992.

[41] S. Toxvaerd. Hamiltonians for discrete dynamics. *Phys. Rev. E*, 50:2271–2274, 1994.

[42] F.J. Vesely. *Computational Physics. An Introduction.* Plenum Press, New York, 1994.

[43] M. Tuckerman, B.J. Berne, and G.J. Martyna. Reversible multiple time scale molecular dynamics. *J. Chem. Phys.*, 97:1990–2001, 1992.

[44] J.C. Sexton and D.H. Weingarten. Hamiltonian evolution for the hybrid Monte Carlo algorithm. *Nucl. Phys. B*, 380:665–677, 1992.

[45] H. Yoshida. Symplectic integrators for hamiltonian systems: Basic theory. In S. Ferraz-Mello, editor, *Chaos, resonance and collective dynamical phenomena in the solar system*, pages 407–411. Kluwer, Dordrecht, 1992.

[46] H. Yoshida. Recent progress in the theory and application of symplectic integrators. *Celes. Mech. Dyn. Astron.*, 56:27–43, 1993.

[47] P. Saha and S. Tremaine. Symplectic integrators for solar system dynamics. *Atron. J.*, 104:1633–1640, 1992.

[48] W. G. Hoover and F. H. Ree, J. Chem. Phys. **47**, 4873 (1967).

[49] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, (2nd edition), London, 1986).

[50] W.F. van Gunsteren, P. K. Weiner, and A. J. Wilkinson, *Computer simulation of biomolecular systems: theoretical and experimental applications* (Escom, Leiden, 1993).

[51] D. Frenkel and A. J. C. Ladd, J. Chem. Phys. **81**, 3188 (1984).

[52] E. J. Meijer, D. Frenkel, R. A. LeSar, and A. J. C. Ladd, J. Chem. Phys. **92**, 7570 (1990).

[53] E.J.Meijer and D.Frenkel, Journal of Chemical Physics **94**, 2269 (1991).

[54] D. Frenkel and B. M. Mulder, Mol. Phys. **55**, 1171 (1985).

[55] A. Stroobants, H. N. W. Lekkerkerker, and D. Frenkel, Phys. Rev. **A36**, 2929 (1987).

[56] D. Frenkel, H. N. W. Lekkerkerker, and A. Stroobants, Nature **332**, 822 (1988).

[57] J.A.C.Veerman and D.Frenkel, Phys. Rev. **A43**, 4334 (1991).

[58] J. A. C. Veerman and D. Frenkel, Phys. Rev. **A41**, 3237 (1990).

[59] J. A. C. Veerman and D. Frenkel, Phys. Rev. **A45**, 5633 (1992).

[60] W.G.T.Kranendonk and D.Frenkel, Mol. Phys. **72**, 679 (1991).

[61] M. D. Eldridge, P. A. Madden, and D. Frenkel, Nature **365**, 35 (1993).

[62] W. G. T. Kranendonk and D. Frenkel, Mol. Phys. **72**, 699 (1991).

[63] M. D. Eldridge, P. A. Madden, and D. Frenkel, Mol. Phys. **79**, 105 (1993).

[64] M.D. Eldridge, P.A. Madden, and D.Frenkel, Mol. Phys. **80**, 987 (1993).

[65] D. A. Kofke, Mol. Phys. **78**, 1331 (1993).

[66] D. A. Kofke, J. Chem. Phys. **98**, 4149 (1993).

[67] P.G. Bolhuis, M.H.J. Hagen, and D. Frenkel, Phys. Rev. E **50**, 4880 (1994).

[68] M.H.J. Hagen, E.J. Meijer, G.C.A.M. Mooij, D. Frenkel, and H.N.W. Lekkerkerker, Nature **365**, 425 (1993).

[69] E.J. Meijer and D. Frenkel, J. Chem. Phys. **100**, 6873 (1994).

[70] M.H.J. Hagen and D. Frenkel, J. Chem. Phys. **101**, 4093 (1994).

[71] P.G. Bolhuis and D. Frenkel, J. Chem. Phys. **101**, 9869 (1994).

[72] R. Agrawal and D.A. Kofke, Phys. Rev. Lett. **74**, 122 (1995).

[73] B. Widom. Some topics in the theory of fluids. *J. Chem. Phys.*, 39:2802–2812, 1963.

[74] B. Widom. Structure of interfaces from uniformity of the chemical potential. *J. Stat. Phys.*, 19:563–574, 1978.

[75] K.S. Shing. Infinite-dilution activity coefficients from computer simulation. *Chem. Phys. Lett.*, 119:149–151, 1985.

[76] P. Sindzingre, G. Ciccotti, C. Massobrio, and D. Frenkel. Partial enthalpies and related quantities in mixtures from computer simulation. *Chem. Phys. Lett.*, 136:35–41, 1987.

[77] D. Frenkel. Free energy computations and first order phase transitions. In G. Ciccotti and W.G. Hoover, editors, *Molecular Dynamics Simulations of Statistical Mechanics Systems*, pages 151–188, Amsterdam, 1986. Proceedings of the 97th Int. 'Enrico Fermi' School of Physics, North Holland.

[78] R. Lustig. Statistical mechanics in the classical molecular dynamics ensemble. I. Fundamentals. *J. Chem. Phys.*, 101:3048–3059, 1994.

[79] R. Lustig. Statistical thermodynamics in the classical molecular dynamics ensemble. II. Application to computer simulation. *J. Chem. Phys.*, 101:3060–3067, 1994.

[80] D.J. Adams. Chemical potential of hard-sphere fluids by Monte Carlo methods. *Mol. Phys.*, 28:1241–1252, 1974.

[81] U. Heinbruch and J. Fischer. On the application of Widom's test particle method to homogeneous and inhomogeneous fluids. *Mol. Simul.*, 1:109–120, 1987.

[82] J.I. Siepmann, I.R. McDonald, and D. Frenkel. Finite-size corrections to the chemical potential. *J. Phys.: Condens. Matter*, 4:679–691, 1992.

[83] K. Shing and S.T. Chung. Computer simulation methods for the calculation of the solubility in supercritical extraction systems. *J. Phys. Chem.*, 91:1674–1681, 1987.

[84] P. Sindzingre, C. Massobrio, G. Ciccotti, and D. Frenkel. Calculation of partial enthalpies of an Argon-Krypton mixture by NPT molecular dynamics. *Chem. Phys.*, 129:213–224–41, 1989.

[85] K.S. Shing and K.E. Gubbins. Free energy and vapour-liquid equilibria for a quadrupolar Lennard-Jones fluid. *Mol. Phys.*, 46:1109–1128, 1982.

[86] K.S. Shing and K.E. Gubbins. The chemical potential in non-ideal liquid mixtures: Computer simulation and theory. *Mol. Phys.*, 49:1121–1138, 1983.

[87] C.H. Bennett. Efficient estimation of free energy differences form Monte Carlo data. *J. Comp. Phys*, 22:245–268, 1976.

[88] P.G. de Gennes, *The physics of liquid crystals* (Oxford University Press, Oxford, 1974).

[89] J.M. Yeomans, *Statistical Mechanics of Phase transitions* (Oxford Science Publications, Oxford, 1992).

[90] D. Chandler, *An Introduction to Modern Statistical Mechanics* (Oxford University Press, New York, 1987).

[91] G. Ciccotti and W.G. Hoover, *Proceedings of the 97th international school of Physics 'Enrico Fermi' on molecular-dynamics simulations of statistical-mechanical systems* (North-Holland, Amsterdam, 1986).

[92] G. Ciccotti, in *Proceedings of the NATO ASI on Computer Simulation in Materials Science*, edited by M. Meyer and V. Pontikis (Kluwer, Dordrecht, 1991), pp. 119–137.

[93] C. H. Bennett, in *Diffusion in solids: Recent developments*, edited by A. S. Nowick and J. J. Burton (Academic Press, New York, 1975), pp. 73–113.