Mode-coupling theory

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Mode-coupling theory

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Abstract. In this set of lecture notes we review the mode-coupling theory of the glass transition from several perspectives. First, we derive mode-coupling equations for the description of density fluctuations from microscopic considerations with the use the Mori–Zwanzig projection operator technique. We also derive schematic mode-coupling equations of a similar form from a field-theoretic perspective. We review the successes and failures of mode-coupling theory, and discuss recent advances in the applications of the theory.

Keywords: dynamical heterogeneities (theory), mode coupling theory, supercooled liquids (theory), slow relaxation and glassy dynamics

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1. Important phenomenology for mode-coupling theory

Since our objective will be to sketch a derivation of what we will call mode-coupling theory (MCT), we will focus our attention on one observable in particular, namely density fluctuations. For this we will first define some of the concepts needed to do so.

We want to calculate a specific time correlation function. In general, such a function is expressed as follows:

$$C(t) = \langle A(t)A(0)\rangle. \tag{1}$$

It is an ensemble average of the evolution of the fluctuations of a variable in time, at equilibrium. As seen in figure 1, $A(t)$ fluctuates around its average value in equilibrium, while $C(t)$ measures the correlation of A at one time with the value of A at another time.

The density or particles in a liquid can be one example of $A(t)$,

$$\rho(\mathbf{r}, t) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i(t)), \tag{2}$$

which we can Fourier transform,

$$\rho_{\mathbf{k}}(t) = \sum_i \int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}}\delta(\mathbf{r} - \mathbf{r}_i(t)),$$
$$= \sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i(t)}. \tag{3}$$

In this case the correlation function will be labelled $F(\mathbf{k}, t)$, which is can be expressed as follows:

$$F(k, t) = \frac{1}{N}\langle \rho_{-\mathbf{k}}(0)\rho_{\mathbf{k}}(t)\rangle = \frac{1}{N}\sum_{ij}\langle e^{-i\mathbf{k}\cdot\mathbf{r}_i(0)}e^{i\mathbf{k}\cdot\mathbf{r}_j(t)}\rangle. \tag{4}$$
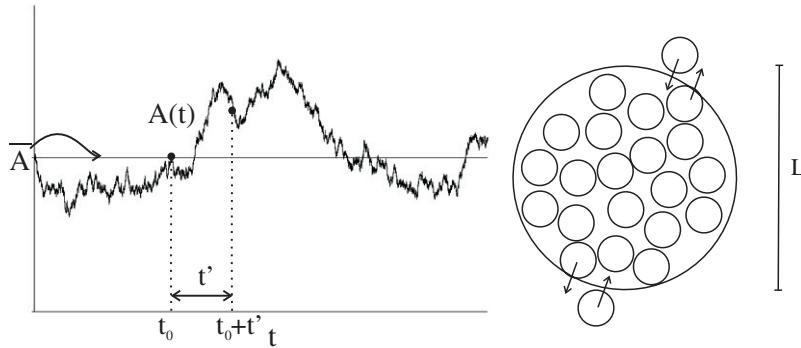
Figure 1. Left: time evolution of the instantaneous fluctuations of the quantity A. The product of fluctuations separated by time t', averaged over all t_0s, gives the correlation function $C(t')$, at equilibrium. Right: fluctuations of the density on length scale $L \sim 2\pi/k$; if k is small, the area of density fluctuations is large.

Note that we need to have $\sum_i \mathbf{k}_i = 0$ (i.e. $-\mathbf{k}+\mathbf{k} = 0$!) to conserve momentum; otherwise the correlation function is equal to zero.

The variables labelled with $\mathbf{k}$ measure density fluctuations in reciprocal ('$k = |\mathbf{k}|$') space, which can be thought of as the inverse length. When k is small we are looking at long length scales, as we can see in figure 1. When it is large, we are probing very short scales.

The function $F(k,t)$ is essentially what scattering experiments measure. At $t = 0$,

$$F(k,t=0) = \frac{1}{N}\langle \rho_{-\mathbf{k}}(0)\rho_{\mathbf{k}}(0)\rangle \equiv S(k), \tag{5}$$

where $S(k)$ is called the static structure factor of the liquid. Why that name? Consider the radial distribution function of a liquid $g(r)$. The function $g(r)$ is proportional to the probability that a particle is a distance r away from a particle at the origin. In a dense liquid, $g(r)$ shows the structure of the solvation shells as depicted in figure 2. Also, it can be shown that [1]–[3]

$$S(k) = 1 + \rho \int \mathrm{d}\mathbf{r}\, \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}} g(\mathbf{r}), \tag{6}$$

where $\rho = N/V$ is the density of the system, and thus $S(k)$ is also indicating something about the liquid structure [1]–[3]. An example for a simple liquid is depicted in figure 2.

But how do we expect $F(k,t)$ to behave? For high temperatures—above the melting point—$F(k,t)$ will decay like a single-exponential function in time for $k \geq 2\pi/\sigma$ as plotted in figure 3. For supercooled liquids, the situation is different and a characteristic decay pattern can also be seen in figure 3. We observe a multi-step relaxation.

(1) At short times decay is coming from free and collisional events that involve local particle motion. Consistent with a short-time expansion, $F(k,t) \sim S(k) - A(k)t^2 + \cdots$ in this regime [1]–[3]. This will be true at any temperature. We will not be concerned much with this part of the decay.
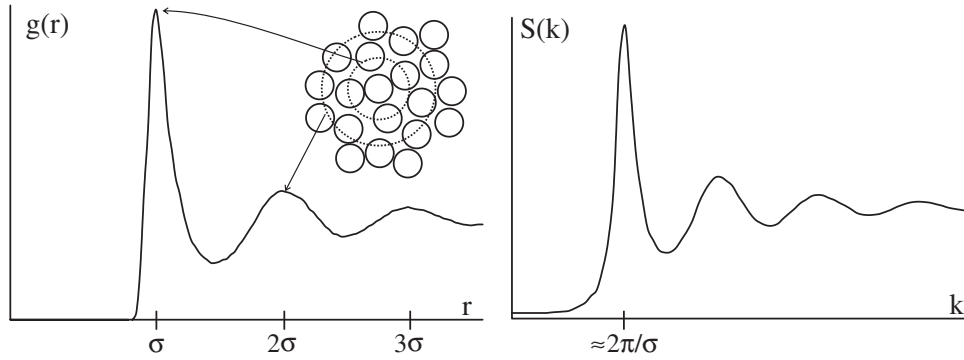
Figure 2. Left: radial distribution function $g(r)$ for a simple liquid of size σ. Right: the corresponding structure factor $S(k)$. A sample structure is also depicted where the solvation shells are indicated by the dotted lines. The exclusion radius can be seen in the absence of amplitude of $g(r)$ for $r \ll \sigma$.
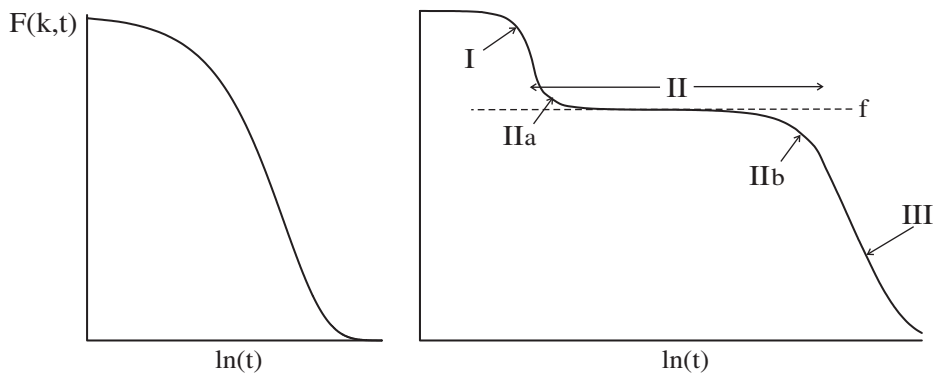
Figure 3. Left: $F(k,t)$ exhibiting exponential $\mathrm{e}^{-t/\tau}$ decay for a normal liquid. Right: supercooled liquids do not have such a simple decay. The various temporal regimes are described in the text. Notice the logarithmic scale.

(2) Intermediate times encompass a period during which particles appear trapped in cages formed by other particles. This regime is the β-relaxation regime. The decay to the plateau (IIa) may be fitted as $f + At^{-a}$ and the decay from the plateau (IIb) as $f - Bt^b$. Also, the exponents have a scaling *consistent* with the relationship

$$\frac{\Gamma(1-a)^2}{\Gamma(1-2a)} = \frac{\Gamma(1+b)^2}{\Gamma(1+2b)}. \tag{7}$$

(3) At long times, in the α-relaxation regime, the decay may be fitted to a stretched exponential law [4]

$$F(k,t) \sim \mathrm{e}^{-(t/\tau)^\beta} \tag{8}$$

with $0 < \beta < 1$. Do not be confused by the notation. It is the β power that appears in the α-relaxation regime! In general β and τ will be k and temperature dependent.

In a later section, we will return to this kind of phenomenology. For now, we just make a few superficial remarks about things that will be covered in more depth by others in these lectures.

The constant τ that appears in the stretched exponential decay law is strongly temperature dependent. All transport coefficients—D (diffusion), η (viscosity), etc—are strongly temperature dependent as well. Over a rather wide range of temperatures, a fit to this temperature dependence may be [4]

$$\eta \sim e^{E/(T-T_0)}. \tag{9}$$

Clearly, as T_0 is approached, relaxation times become so large that the system cannot stay in equilibrium. Other fitting forms, some that do not imply a divergence at finite temperatures, may be used to fit the data as well.

Some systems, hard spheres for example, are not characterized by temperature, but by density of the packing fraction $\phi = \frac{4}{3}\pi a^3 \rho$, where a is the particle radius. For such systems, one may fit with [4]

$$\eta \sim e^{B/(\phi-\phi_c)}, \tag{10}$$

or with other forms.

2. The mode-coupling theory of density fluctuations

Our strategy will be to derive an *exact* equation of motion for $F(k,t)$ and then to make approximations that allow us to solve them [5, 6]. The approximations are uncontrolled, and we will judge them by their success or failure.

2.1. Memory functions

Consider some classical function of phase space variables $A(t)$, where the time dependence originates from that of the positions $\mathbf{r}_i$ and of the momenta $\mathbf{p}_i$ for an N-particle system. We know from Hamilton's equations that

$$\frac{\mathrm{d}A(t)}{\mathrm{d}t} = \{A(t), \mathcal{H}\} \equiv \mathrm{i}\mathcal{L}A(t), \tag{11}$$

where $\{,\}$ is a classical Poisson bracket, which can be expressed as follows:

$$\{A, B\} \equiv \sum_i \left(\frac{\partial A}{\partial \mathbf{r}_i} \cdot \frac{\partial B}{\partial \mathbf{p}_i} - \frac{\partial A}{\partial \mathbf{p}_i} \cdot \frac{\partial B}{\partial \mathbf{r}_i} \right). \tag{12}$$

Also, for liquids of interest, $\mathcal{H}$ is a classical Hamiltonian with pairwise interactions $\phi(r)$ between the particles,

$$\mathcal{H} = \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{i,j \neq i} \phi(\mathbf{r}_{ij}). \tag{13}$$

We can thus identify the following:

$$\mathrm{i}\mathcal{L} = \frac{1}{m} \sum_i \left(\mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} \right) - \sum_{i,j \neq i} \left(\frac{\partial \phi(\mathbf{r}_{ij})}{\partial \mathbf{r}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} \right). \tag{14}$$

It would be possible to integrate the differential equation to find $A(t) = e^{\mathrm{i}\mathcal{L}t}A(0)$, but this is not useful by itself.
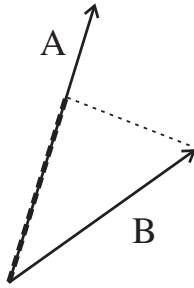
Figure 4. A two-dimensional version of the projection operator $\mathcal{P}B$. The quantity B is projected unto the space A, which extracts the A component of B (indicated by a thick dashed line).

We also need to define a scalar product of the variables as

$$(A, B) \equiv \langle A^* B \rangle. \tag{15}$$

Now, consider an operator called a *projection operator* $\mathcal{P}$ [1]–[3], [5, 6],

$$\mathcal{P} \equiv (A, \ldots)(A, A)^{-1} A. \tag{16}$$

If A is a vector, $(A, A)^{-1}$ is thus the inverse of a matrix. Note also that $\mathcal{P}^2 A = \mathcal{P}A = A$. In geometrical terms, the projection operator finds the component of some variable B along the chosen direction A, as depicted in figure 4.

This is useful, as we can extract from an arbitrary B how much 'character' of A it has. In particular, the operator A may be a slowly varying (quasi-hydrodynamic) variable. Consider the density as defined in equation (4),

$$\rho_{\mathbf{k}}(t) = \sum_i e^{i\mathbf{k} \cdot \mathbf{r}_i(t)},$$

and then

$$\dot{\rho}_{\mathbf{k}}(t) = i\mathbf{k} \cdot \sum_i \frac{\mathbf{p}_i(t)}{m} e^{i\mathbf{k} \cdot \mathbf{r}_i(t)} = i\mathbf{k} \cdot \mathbf{j}_{\mathbf{k}}(t) = i|\mathbf{k}|j_{\mathbf{k}}^L(t), \tag{17}$$

where $j_{\mathbf{k}}^L(t)$ is the longitudinal current. If k is small (large length scales), then $\dot{\rho}_{\mathbf{k}}(t)$ is approximately small. This is what is meant by *slow*. In the limit $k = 0$, then $\dot{\rho}_{k=0} = 0$, and the density is strictly conserved. As figure 1 indicates, if k is small, the area of density fluctuations is large, i.e. the rate at which the number of particles fluctuates is small.

We now want to find the exact equation of motion for a correlation function

$$\frac{d\underline{A}(t)}{dt} = e^{i\mathcal{L}t} \overbrace{[\mathcal{P} + (1 - \mathcal{P})]}^{=1} i\mathcal{L}\underline{A},$$
$$= i\underline{\Omega} \cdot \underline{A}(t) + e^{i\mathcal{L}t}(1 - \mathcal{P})i\mathcal{L}\underline{A}, \tag{18}$$

where

$$i\underline{\Omega} = (\underline{A}, i\mathcal{L}\underline{A}) \cdot (\underline{A}, \underline{A})^{-1}. \tag{19}$$

Now, writing

$$e^{i\mathcal{L}t} = e^{i\mathcal{L}t}\mathcal{O}(t) + e^{i(1-\mathcal{P})\mathcal{L}t}, \tag{20}$$

$\mathcal{O}(t)$ can be obtained by differentiating both sides of the equation:

$$i\mathcal{L}e^{i\mathcal{L}t} = i\mathcal{L}e^{i\mathcal{L}t}\mathcal{O}(t) + e^{i\mathcal{L}t}\dot{\mathcal{O}}(t) + i[(1-\mathcal{P})\mathcal{L}]e^{i(1-\mathcal{P})\mathcal{L}t},$$
$$i\mathcal{L}(e^{i\mathcal{L}t}\mathcal{O}(t) + e^{i(1-\mathcal{P})\mathcal{L}t}) = i\mathcal{L}e^{i\mathcal{L}t}\mathcal{O}(t) + e^{i\mathcal{L}t}\dot{\mathcal{O}}(t) + i[(1-\mathcal{P})\mathcal{L}]e^{i(1-\mathcal{P})\mathcal{L}t},$$
$$i\mathcal{L}\mathcal{O}(t) + e^{i(1-\mathcal{P})\mathcal{L}t} = e^{i\mathcal{L}t}\dot{\mathcal{O}}(t) + i[(1-\mathcal{P})\mathcal{L}]e^{i(1-\mathcal{P})\mathcal{L}t},$$
$$e^{i\mathcal{L}t}\dot{\mathcal{O}}(t) = i\mathcal{P}\mathcal{L}e^{i(1-\mathcal{P})\mathcal{L}t},$$
$$\mathcal{O}(t) = i\int_0^t d\tau\, e^{i\mathcal{L}t}\mathcal{P}\mathcal{L}e^{i(1-\mathcal{P})\mathcal{L}\tau}, \tag{21}$$

where the last equality follows from the fact that $\mathcal{O}(0) = 0$. As a result, we may write

$$e^{i\mathcal{L}t}i(1-\mathcal{P})\mathcal{L}\underline{A} = \int_0^t d\tau\, e^{i\mathcal{L}(t-\tau)}i\mathcal{P}\mathcal{L}f(\tau) + f(t), \tag{22}$$

where $f(t)$ is called the *fluctuating force*:

$$f(t) \equiv e^{i(1-\mathcal{P})\mathcal{L}t}i(1-\mathcal{P})\mathcal{L}\underline{A}. \tag{23}$$

What does this mean? The fluctuating force is obtained by taking the time derivative of $\underline{A}$, using the complementary projection operator $(1-\mathcal{P})$ to remove the 'A' character—perhaps the *slow* character—and is then propagated in the orthogonal—*fast*—space. To put it another way, if $\mathcal{P}$ removes the slow character from a variable, then the fluctuating force is the remaining fast force. We will come back to this later.

It can be shown that $(\underline{A}, f(t)) = 0$, by noticing that the definition of $f(t)$ contains the $(1-\mathcal{P})$ factor. This means that $f(t)$ is orthogonal to $\underline{A}$, in accord with the discussion above. Noting that

$$i(\underline{A}, \mathcal{L}f(t)) = i(\mathcal{L}\underline{A}, f(t)) = i((1-\mathcal{P})\mathcal{L}\underline{A}, f(t)) = -(f(0), f(t)), \tag{24}$$

the first term on the RHS of equation (22) allows the equation of motion to be rewritten as

$$\frac{d\underline{A}(t)}{dt} = i\underline{\Omega} \cdot \underline{A}(t) - \int_0^t d\tau\, \underline{K}(\tau) \cdot \underline{A}(t-\tau) + f(t), \tag{25}$$

where we define the *memory function* $\underline{K}(t)$:

$$\underline{K}(t) \equiv (f, f(t)) \cdot (\underline{A}, \underline{A})^{-1}. \tag{26}$$

This is a fundamental and exact equation for the time dependence of $\underline{A}(t)$.

Defining the correlation matrix

$$\underline{C}(t) \equiv \langle \underline{A}^*(0)\underline{A}(t) \rangle = (\underline{A}, \underline{A}(t)) \tag{27}$$

and using the equality $(\underline{A}, f(t)) = 0$, we get

$$\frac{d\underline{C}(t)}{dt} = i\underline{\Omega} \cdot \underline{C}(t) - \int_0^t d\tau\, \underline{K}(\tau) \cdot \underline{C}(t-\tau) \tag{28}$$

as an exact equation for the matrix of correlation functions $\underline{C}(t)$ that we will want to compute. The problem with computing $\underline{C}(t)$ is embodied in the difficulty of determining $\underline{K}(t)$.

Now, we want to focus this general framework on density fluctuations with respect to the bulk density ρ, which will allow us to get an expression for the intermediate scattering function. Consider [3]

$$\underline{A} = \begin{bmatrix} \delta\rho_{\mathbf{q}} \\ j_{\mathbf{q}}^L \end{bmatrix}, \tag{29}$$

where

$$\delta\rho_{\mathbf{q}} = \sum_i e^{i\mathbf{q}\cdot\mathbf{r}_i} - (2\pi)^3 \rho\delta(\mathbf{q}),$$
$$j_{\mathbf{q}}^L = \frac{1}{m}\sum_i (\hat{\mathbf{q}}\cdot\mathbf{p}_i)e^{i\mathbf{q}\cdot\mathbf{r}_i}, \tag{30}$$

and therefore

$$\begin{aligned}
\underline{C}(t) &= \langle \underline{A}^* \underline{A}(t) \rangle \\
&= \begin{bmatrix} \langle \delta\rho_{-\mathbf{q}}\delta\rho_{\mathbf{q}}(t) \rangle & \langle \delta\rho_{-\mathbf{q}} j_{\mathbf{q}}^L(t) \rangle \\ \langle j_{-\mathbf{q}}^L \delta\rho_{\mathbf{q}}(t) \rangle & \langle j_{-\mathbf{q}}^L j_{\mathbf{q}}^L(t) \rangle \end{bmatrix}.
\end{aligned} \tag{31}$$

For the purpose of this demonstration, we will concentrate on the element in the lower left corner of the matrix, which is in this case $(N/iq)(\mathrm{d}^2 F(q,t)/\mathrm{d}t^2)$. At $t = 0$, the matrix reduces to

$$\underline{C}(0) = \begin{bmatrix} NS(q) & 0 \\ 0 & \dfrac{Nk_{\mathrm{B}}T}{m} \end{bmatrix}. \tag{32}$$

Also,

$$\begin{aligned}
i\underline{\Omega} &= \langle \underline{A}^* \underline{\dot{A}} \rangle \cdot \langle \underline{A}^* \underline{A} \rangle^{-1}, \\
&= \begin{bmatrix} \langle \delta\rho_{-\mathbf{q}}\delta\dot{\rho}_{\mathbf{q}} \rangle & \left\langle \delta\rho_{-\mathbf{q}}\dfrac{\mathrm{d}j_{\mathbf{q}}^L}{\mathrm{d}t} \right\rangle \\ \langle j_{-\mathbf{q}}^L \delta\dot{\rho}_{\mathbf{q}} \rangle & \left\langle \dfrac{\mathrm{d}j_{-\mathbf{q}}^L}{\mathrm{d}t}\delta\dot{\rho}_{\mathbf{q}} \right\rangle \end{bmatrix} \cdot \langle \underline{A}^* \underline{A} \rangle^{-1}, \\
&= \begin{bmatrix} 0 & i\dfrac{Nqk_{\mathrm{B}}T}{m} \\ i\dfrac{Nqk_{\mathrm{B}}T}{m} & 0 \end{bmatrix} \cdot \begin{bmatrix} \dfrac{1}{NS(q)} & 0 \\ 0 & \dfrac{m}{Nk_{\mathrm{B}}T} \end{bmatrix}, \\
&= \begin{bmatrix} 0 & iq \\ i\dfrac{qk_{\mathrm{B}}T}{mS(q)} & 0 \end{bmatrix}.
\end{aligned} \tag{33}$$

To obtain the last two equations, we used integration by parts, the property that the correlation of an observable and its derivative is always zero, and the statistical

thermodynamics result that follows:

$$\langle j^L_{-\mathbf{q}}\delta\dot\rho_{\mathbf{q}}\rangle = \frac{\mathrm{i}}{m^2}\sum_{i,j}\langle(\hat{\mathbf{q}}\cdot\mathbf{p}_i)\mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}_i}(\mathbf{q}\cdot\mathbf{p}_j)\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_j}\rangle,$$

$$= \frac{\mathrm{i}q}{m}\sum_i\langle mv_i^2\rangle = \mathrm{i}\frac{Nqk_{\mathrm{B}}T}{m}. \tag{34}$$

The random force $f(0)$ is expressed as

$$f(0) = (1-\mathcal{P})\underline{\dot{A}},$$

$$= \begin{bmatrix} \delta\dot\rho_{\mathbf{q}} \\ \dfrac{\mathrm{d}j^L_{\mathbf{q}}}{\mathrm{d}t} \end{bmatrix} - \begin{bmatrix} 0 & \mathrm{i}q \\ \mathrm{i}\dfrac{qk_{\mathrm{B}}T}{mS(q)} & 0 \end{bmatrix}\cdot\begin{bmatrix} \delta\rho_{\mathbf{q}} \\ j^L_{\mathbf{q}} \end{bmatrix},$$

$$= \begin{bmatrix} 0 \\ \dfrac{\mathrm{d}j^L_{\mathbf{q}}}{\mathrm{d}t} - \mathrm{i}\dfrac{qk_{\mathrm{B}}T}{mS(q)}\delta\rho_{\mathbf{q}} \end{bmatrix} \equiv \begin{bmatrix} 0 \\ R_{\mathbf{q}} \end{bmatrix}. \tag{35}$$

We will now look at the equation of motion term by term. First,

$$\frac{\mathrm{d}\underline{C}(t)}{\mathrm{d}t} = \begin{pmatrix} \dfrac{\mathrm{d}}{\mathrm{d}t}\langle\delta\rho_{-\mathbf{q}}\delta\rho_{\mathbf{q}}(t)\rangle & \dfrac{\mathrm{d}}{\mathrm{d}t}\langle\delta\rho_{-\mathbf{q}}j^L_{\mathbf{q}}(t)\rangle \\ \dfrac{\mathrm{d}}{\mathrm{d}t}\langle j^L_{-\mathbf{q}}\delta\rho_{\mathbf{q}}(t)\rangle & \dfrac{\mathrm{d}}{\mathrm{d}t}\langle j^L_{-\mathbf{q}}j^L_{\mathbf{q}}(t)\rangle \end{pmatrix}. \tag{36}$$

Note that the lower left corner term equals $(N/\mathrm{i}q)(\mathrm{d}^2F(q,t)/\mathrm{d}t^2)$. Second,

$$\mathrm{i}\underline{\Omega}\cdot\underline{C}(t) = \begin{bmatrix} 0 & \mathrm{i}q \\ \mathrm{i}\dfrac{qk_{\mathrm{B}}T}{mS(q)} & 0 \end{bmatrix}\cdot\begin{bmatrix} \langle\delta\rho_{-\mathbf{q}}\delta\rho_{\mathbf{q}}(t)\rangle & \langle\delta\rho_{-\mathbf{q}}j^L_{\mathbf{q}}(t)\rangle \\ \langle j^L_{-\mathbf{q}}\delta\rho_{\mathbf{q}}(t)\rangle & \langle j^L_{-\mathbf{q}}j^L_{\mathbf{q}}(t)\rangle \end{bmatrix}. \tag{37}$$

Notice the lower left corner term is $-(qNk_{\mathrm{B}}T/\mathrm{i}mS(q))F(q,t)$ this time. Lastly, the memory matrix is

$$\underline{K}(t) = \left\langle\begin{bmatrix} 0 \\ R^*_{\mathbf{q}} \end{bmatrix}\cdot[\,0 \quad R_{\mathbf{q}}(t)\,]\right\rangle\cdot\langle\underline{A}^*\underline{A}\rangle^{-1},$$

$$= \begin{bmatrix} 0 & 0 \\ 0 & \langle R_{-\mathbf{q}}R_{\mathbf{q}}(t)\rangle \end{bmatrix}\cdot\begin{bmatrix} \dfrac{1}{NS(q)} & 0 \\ 0 & \dfrac{m}{Nk_{\mathrm{B}}T} \end{bmatrix},$$

$$= \begin{bmatrix} 0 & 0 \\ 0 & \dfrac{m\langle R_{-\mathbf{q}}R_{\mathbf{q}}(t)\rangle}{Nk_{\mathrm{B}}T} \end{bmatrix}. \tag{38}$$

Concentrating on the lower left corner, using the equation of motion from equation (27), we find [1]–[3], [5]

$$\frac{\mathrm{d}^2F(q,t)}{\mathrm{d}t^2} + \frac{q^2k_{\mathrm{B}}T}{mS(q)}F(q,t) + \frac{m}{Nk_{\mathrm{B}}T}\int_0^t\mathrm{d}\tau\,\langle R_{-\mathbf{q}}R_{\mathbf{q}}(\tau)\rangle\frac{\mathrm{d}}{\mathrm{d}t}F(q,t-\tau) = 0. \tag{39}$$

This equation is exact, but impossible to solve. To make approximations, we will look at $\langle R_{-\mathbf{q}} R_{\mathbf{q}}(t) \rangle$ using some intuition. Recall that

$$R_{\mathbf{q}} = \frac{\mathrm{d}j_{\mathbf{q}}^L}{\mathrm{d}t} - \mathrm{i}\frac{qk_{\mathrm{B}}T}{mS(q)}\delta\rho_{\mathbf{q}} \tag{40}$$

and that

$$\begin{aligned}
\frac{\mathrm{d}j_{\mathbf{q}}^L}{\mathrm{d}t} &= \frac{\mathrm{d}}{\mathrm{d}t}\left\{\frac{1}{m}\sum_i (\hat{\mathbf{q}}\cdot\mathbf{p}_i)\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_i}\right\}, \\
&= \frac{1}{m}\sum_i \left(\hat{\mathbf{q}}\cdot\frac{\mathrm{d}\mathbf{p}_i}{\mathrm{d}t}\right)\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_i} + \frac{\mathrm{i}}{m^2}\sum_i (\hat{\mathbf{q}}\cdot\mathbf{p}_i)^2\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_i}.
\end{aligned} \tag{41}$$

Also, note that in this last equation $\mathrm{d}\mathbf{p}_i/\mathrm{d}t$ is a force and therefore

$$\frac{\mathrm{d}\mathbf{p}_i}{\mathrm{d}t} \sim -\sum_{i\neq j}\nabla\phi(|\mathbf{r}_i - \mathbf{r}_j|) = \sum_{\mathbf{k}}\mathrm{i}\mathbf{k}\phi_{\mathbf{k}}\delta\rho_{\mathbf{k}}\delta\rho_{-\mathbf{k}}, \tag{42}$$

where we made the momentum space transformation $\phi_{\mathbf{k}} = \int \mathrm{d}\mathbf{r}\,\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}\phi(\mathbf{r})$. We then see that hidden in the fluctuating force is a pair of densities. This illustrates an important point: at first, we may have suspected that the fluctuating force is a *fast* variable and that it decays on a short timescale because we removed the slow modes $\delta\rho_{\mathbf{k}}$ from it—but we see that it contains, at leading order, a slow character (at least if $\delta\rho_{\mathbf{k}}$ is slow) from the product of slow modes $\delta\rho_{\mathbf{k}}\delta\rho_{-\mathbf{k}}$! Overall the time derivative of the current has the symmetry of $\delta\rho_{\mathbf{k}}\delta\rho_{\mathbf{q}-\mathbf{k}}$, where the $\mathbf{q}$ factor comes from $\sum_i \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_i}$ that multiplies the force in equation (41).

We will now approximate $\langle R_{-\mathbf{q}}\mathrm{e}^{\mathrm{i}\mathcal{Q}\mathcal{L}t}R_{\mathbf{q}}\rangle$. As a convention, note that $\mathcal{Q} \equiv 1 - \mathcal{P}$.

(1) Make the replacement $\mathrm{e}^{\mathrm{i}\mathcal{Q}\mathcal{L}t} \rightarrow \mathcal{P}_2\mathrm{e}^{\mathrm{i}\mathcal{L}t}\mathcal{P}_2$, where we define the new projection operator

$$\mathcal{P}_2 \equiv \sum_{\mathbf{k_1},\mathbf{k_2},\mathbf{k_3},\mathbf{k_4}} A_{\mathbf{k_1},\mathbf{k_2}}\langle A^*_{\mathbf{k_3},\mathbf{k_4}}\ldots\rangle\langle A^*_{\mathbf{k_1},\mathbf{k_2}}A_{\mathbf{k_3},\mathbf{k_4}}\rangle^{-1} \tag{43}$$

and where $A_{\mathbf{k_1},\mathbf{k_2}} = \delta\rho_{\mathbf{k_1}}\delta\rho_{\mathbf{k_2}}$. The $\mathcal{P}_2$ operator simply projects $R_{\mathbf{q}}$ onto its dominant slow product mode. We neglect the $\mathcal{Q}$ in the exponent, simply because it is hard to compute anything keeping it there. However, to $\mathcal{O}(q^2)$, it may be shown that this neglect has no consequences.

(2) Factorize four-point density terms into products of two-point ones.

Using this algorithm, we get

$$\mathcal{P}_2 R_{\mathbf{q}} = \sum_{\mathbf{k_1},\mathbf{k_2}} V_{\mathbf{q}}(\mathbf{k_1},\mathbf{k_2})\delta\rho_{\mathbf{k_1}}\delta\rho_{\mathbf{k_2}}, \tag{44}$$

where

$$V_{\mathbf{q}}(\mathbf{k_1},\mathbf{k_2}) \equiv \sum_{\mathbf{k_3},\mathbf{k_4}} \langle \delta\rho_{\mathbf{k_1}}\delta\rho_{\mathbf{k_2}}R_{\mathbf{q}}\rangle \cdot \langle \delta\rho_{\mathbf{k_1}}\delta\rho_{\mathbf{k_2}}\delta\rho_{\mathbf{k_3}}\delta\rho_{\mathbf{k_4}}\rangle^{-1}. \tag{45}$$

The denominator has a product of four density variables that will be factorized into products of two structure factors. The numerator has terms like

$$\left\langle \delta\rho_{-\mathbf{k}}\delta\rho_{\mathbf{k}-\mathbf{q}}\frac{\mathrm{d}j_{\mathbf{q}}^{L}}{\mathrm{d}t}\right\rangle = -\langle\delta\dot\rho_{-\mathbf{k}}\delta\rho_{\mathbf{k}-\mathbf{q}}j_{\mathbf{q}}^{L}\rangle - \langle\delta\rho_{-\mathbf{k}}\delta\dot\rho_{\mathbf{k}-\mathbf{q}}j_{\mathbf{q}}^{L}\rangle, \tag{46}$$

where the result was obtained by integration by parts, and

$$-\frac{\mathrm{i}qk_{\mathrm{B}}T}{mS(q)}\langle\delta\rho_{-\mathbf{k}}\delta\rho_{\mathbf{k}-\mathbf{q}}\delta\rho_{\mathbf{q}}\rangle. \tag{47}$$

Let us calculate one of the terms in equation (46),

$$-\langle\delta\dot\rho_{-\mathbf{k}}\delta\rho_{\mathbf{k}-\mathbf{q}}j_{\mathbf{q}}^{L}\rangle = \mathrm{i}\left\langle\sum_{i}(\mathbf{k}\cdot\mathbf{p}_i)\mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}_i}\sum_{j}\mathrm{e}^{\mathrm{i}(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_i}\sum_{l}(\hat{\mathbf{q}}\cdot\mathbf{p}_l)\mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}_l}\right\rangle,$$

$$= \mathrm{i}\sum_{ij}\langle\mathrm{e}^{\mathrm{i}(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_j}\mathrm{e}^{\mathrm{i}(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}_i}\rangle\frac{k_{\mathrm{B}}T}{m}(\mathbf{k}\cdot\hat{\mathbf{q}}),$$

$$= \mathrm{i}(\mathbf{k}\cdot\hat{\mathbf{q}})\frac{k_{\mathrm{B}}T}{m}NS(|\mathbf{k}-\mathbf{q}|), \tag{48}$$

where we used the result of equation (34), to complete the calculation. The other term similarly gives

$$-\langle\delta\rho_{-\mathbf{k}}\delta\dot\rho_{\mathbf{k}-\mathbf{q}}j_{\mathbf{q}}^{L}\rangle = \mathrm{i}(\hat{\mathbf{q}}\cdot(\mathbf{q}-\mathbf{k}))\frac{k_{\mathrm{B}}T}{m}NS(k). \tag{49}$$

The term in equation (47) is hard to compute directly, but within the *convolution approximation*, it can be reduced as follows [1, 5]:

$$\langle\delta\rho_{-\mathbf{k}}\delta\rho_{\mathbf{k}-\mathbf{q}}\delta\rho_{\mathbf{q}}\rangle \approx NS(k)S(q)S(|\mathbf{k}-\mathbf{q}|). \tag{50}$$

After treating all static density fluctuations within the Gaussian (and convolution) approximations, we find that the vertex $V_{\mathbf{q}}(\mathbf{k_1},\mathbf{k_2})$ can be expressed as a function of only two wavevectors. As a consequence of translational invariance, we would be left only with terms involving the difference of wavevectors $\mathbf{k}\equiv\mathbf{k_1}-\mathbf{k_2}$, which allows us to write $V_{\mathbf{q}}(\mathbf{k_1},\mathbf{k_2})=V_{\mathbf{k},\mathbf{q}-\mathbf{k}}$. Also note that the summation is now only over $\mathbf{k}$. Combining all terms gives

$$V_{\mathbf{k},\mathbf{q}-\mathbf{k}} = \frac{\mathrm{i}k_{\mathrm{B}}T}{2mN}\left\{\frac{(\hat{\mathbf{q}}\cdot\mathbf{k})}{S(k)}+\frac{\hat{\mathbf{q}}\cdot(\mathbf{q}-\mathbf{k})}{S(|\mathbf{k}-\mathbf{q}|)}-(\mathbf{q}\cdot\hat{\mathbf{q}})\right\},$$

$$= \frac{\mathrm{i}\rho k_{\mathrm{B}}T}{2mN}\{(\hat{\mathbf{q}}\cdot\mathbf{k})c(k)+\hat{\mathbf{q}}\cdot(\mathbf{q}-\mathbf{k})c(|\mathbf{k}-\mathbf{q}|)\}, \tag{51}$$

where we have rewritten the result using the direct correlation function $c(k)\equiv(1/\rho)(1-1/S(k))$. So, piecing this together,

$$\langle(R_{\mathbf{q}}\mathcal{P}_2)^*(\mathcal{P}_2 R_{\mathbf{q}}(t))\rangle \simeq \sum_{\mathbf{k},\mathbf{k}'}|V_{\mathbf{k},\mathbf{q}-\mathbf{k}}^*V_{\mathbf{k}',\mathbf{q}-\mathbf{k}'}|\langle\delta\rho_{-\mathbf{k}'}\delta\rho_{\mathbf{k}'-\mathbf{q}}\delta\rho_{\mathbf{k}}(t)\delta\rho_{\mathbf{q}-\mathbf{k}}(t)\rangle,$$

$$\simeq \sum_{\mathbf{k},\mathbf{k}'}|V_{\mathbf{k},\mathbf{q}-\mathbf{k}}^*V_{\mathbf{k}',\mathbf{q}-\mathbf{k}'}|N^2F(k,t)F(|\mathbf{q}-\mathbf{k}|,t)(\delta_{\mathbf{k},\mathbf{k}'}+\delta_{\mathbf{k}'-\mathbf{q},\mathbf{k}}),$$

$$= \frac{\rho^2(k_{\mathrm{B}}T)^2}{2m^2}\sum_{\mathbf{k}}|\tilde{V}_{\mathbf{q}-\mathbf{k},\mathbf{k}}|^2F(k,t)F(|\mathbf{q}-\mathbf{k}|,t), \tag{52}$$
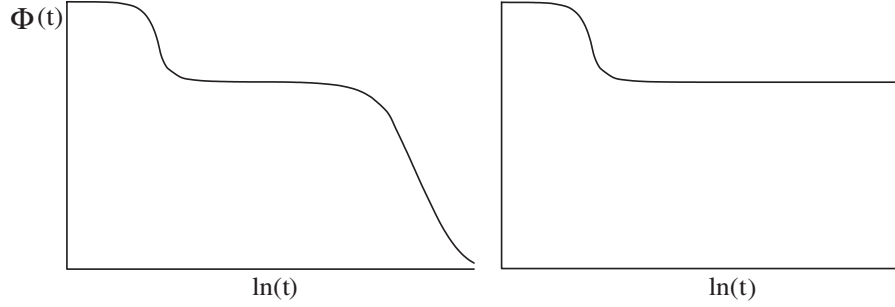
Figure 5. Left: $\Phi(t)$ decay in the ergodic (supercooled) case. The correlation vanishes on a finite timescale. Right: in the non-ergodic (glassy) case, that same function remains finite even for infinite times.

where we used Wick's factorization and where

$$\tilde{V}_{\mathbf{q}-\mathbf{k},\mathbf{k}} \equiv \{(\hat{\mathbf{q}} \cdot \mathbf{k})c(k) + \hat{\mathbf{q}} \cdot (\mathbf{q} - \mathbf{k})c(|\mathbf{q} - \mathbf{k}|)\}. \tag{53}$$

We need to convert the discrete sum to the continuous integral, $\sum_{\mathbf{k}} \to (V/(2\pi)^3) \int d\mathbf{k}$, and multiply by the $m/Nk_{\mathrm{B}}T$ prefactor as obtained in equation (39), to get the final MCT equation:

$$0 = \frac{d^2 F(q,t)}{dt^2} + \frac{q^2 k_{\mathrm{B}}T}{mS(q)}F(q,t) + \int_0^t d\tau \, K(q,t-\tau)\frac{\partial F(q,t)}{\partial \tau} \tag{54}$$

with

$$K(q,t) = \frac{\rho k_{\mathrm{B}}T}{16\pi^3 m} \int d\mathbf{k} \, |\tilde{V}_{\mathbf{q}-\mathbf{k},\mathbf{k}}|^2 F(k,t)F(|\mathbf{k}-\mathbf{q}|,t). \tag{55}$$

2.2. Some properties of the solution(s) of the MCT equation

2.2.1. Schematic MCT. Via the approximation discussed by Bengtzelius *et al* we can reduce our MCT equation to a schematic form,

$$\frac{\partial^2 \Phi(t)}{\partial t^2} + \Omega_0^2 \Phi(t) + \lambda \int_0^t d\tau \, \Phi^2(t-\tau)\frac{\partial \Phi(\tau)}{\partial \tau} = 0, \tag{56}$$

where $\Phi(t) \sim F(k,t)$, before we neglect the coupling wavevectors. The solutions of equation (56) have been discussed by Leutheusser [7] and Bengtzelius *et al* [8]. The most striking feature of this equation, and of the full MCT equation from which we 'derived' it, is that there is a transition to a completely non-ergodic phase for particular Ω_0^2 and λ (or T and ρ for the *real* MCT equation). The two cases are depicted in figure 5.

The transition from ergodic to non-ergodic at a sharp, well-defined set of parameters may be interpreted as the transition from a liquid to a solid. The fact that correlations do not decay as $t \to \infty$ is indicative of this. However, no information of an ordered state was used or imposed. Thus, the solid could only be a disordered one, i.e. *a glass*.

2.2.2. Solutions of full MCT equations. If we denote by T_c the temperature where MCT predicts a glass transition, the relaxation time τ scales as [5]–[8]

$$\tau(q,T) \sim A_q(T - T_c)^{-\gamma}, \tag{57}$$

which means that when $T \to T_c$, τ diverges as a power law with a universal exponent γ. This form may fit data, but only over a limited temperature range.

Also, the decay in the β-relaxation regime is indeed given by [5]–[8]

$$\text{early } \beta: \quad f + At^{-a},$$
$$\text{late } \beta: \quad f - Bt^{b},$$

with

$$\frac{\Gamma(1-a)^2}{\Gamma(1-2a)} = \frac{\Gamma(1+b)^2}{\Gamma(1+2b)}, \tag{58}$$

at least for T very close to T_c, i.e. when $(T - T_c)/T_c \ll 1$. This is a great triumph of the MCT equations and is *fully consistent* with simulations and experiments [5, 6]. Furthermore, the power γ is related to the exponents a and b as

$$\gamma = \frac{1}{2a} + \frac{1}{2b}. \tag{59}$$

For the α-relaxation regime, an approximate solution of the full MCT equations is indeed approximately given by

$$F(k,t) \sim \mathrm{e}^{-(t/\tau_k)^{\beta_k}}, \tag{60}$$

and this stretched exponential function describes well experiments and simulations. The schematic equation, however, only exhibits exponential decay.

More generally, MCT predicts that for a correlator at temperature T a *time–temperature* superposition holds [5, 6]:

$$C(t,T) = \hat{C}(t/\tau(T)), \tag{61}$$

where $C(t,T)$ is a correlation function, $\hat{C}$ is some master function and $\tau(T)$ is the α-relaxation time. This is also generally consistent with experiments and simulations.

2.2.3. Redux: an assessment of the successes and failures of MCT. Even a scientist who is opposed to the spirit and approximations that go into MCT ought to be impressed by its success, where it succeeds. Furthermore, it is essentially the *only* first-principles theory of glassy liquids. That is, from the structure of the liquid alone ($S(k)$, the structure factor) a detailed set of dynamical predictions emerge. We will now spell out where MCT works and where (we think) it does not.

Successes

(1) MCT makes some remarkable predictions that *are* correct. For example, the remarkable scaling properties in the β-relaxation regime that are predicted are essentially correct and so is the time–temperature superposition in the α-relaxation regime. This is similarly accurate for other predictions that we will not discuss here [5, 6].

(2) MCT has predicted novel relaxation patterns correctly. One recent striking example is the behaviour of colloidal suspensions with induced short-ranged attractions [9]. Here, MCT has predicted that adding attractions may melt the glass from hard spheres, and that for certain parameters, logarithmic relaxation may be observed. Both predictions have been confirmed again by computer simulations and experiments.

(3) Although we will not discuss this here, there exist models with quenched disorder (spin-glass models) for which the schematic MCT is *exact* [10, 11]. These models make connections between MCT and energy landscape theories possible, as well as extensions of the MCT approach to situations that are out of equilibrium (ageing). This has been very fruitful and has led to new insights into glassy systems.

Failures

(1) The best-known failure of MCT is that it predicts a sharp glass transition at a temperature T_c, but $T_c > T_g$. This means that MCT predicts kinetic arrest to a non-ergodic phase at temperatures where the system is still ergodic and liquid.

(2) MCT also predicts power-law divergence of transport coefficients and relaxation times as in equation (57), but this is less accurate over a wide range of temperatures than the temperature dependence of transport coefficients given in equation (9) [4]. It is a reasonable fitting form over several decades of relaxation time for mildly supercooled liquids. In addition, the parameters β, a, b, ... are predicted to be constant in MCT, at least for temperatures for $(T - T_c)/T_c \ll 1$. But in actuality, they are mildly temperature dependent. One should be careful, however, not to take asymptotic predictions of MCT and apply them to cases where $(T - T_c)/T_c$ is not small [5].

(3) Another failure of MCT is in the prediction of certain indicators of collective relaxation. In general, timescales and length scales of such heterogeneous motion can be probed by multi-point correlations. A simple, non-multi-point function that seems to correlate crudely with the timescale of such motion is the non-Gaussian parameter

$$\alpha_2(t) = \frac{3\langle r^4(t)\rangle}{5\langle r_2(t)\rangle^2} - 1, \tag{62}$$

where

$$\langle r^2(t)\rangle = \langle [r(t) - r(0)]^2\rangle \tag{63}$$

for a tagged particle and similarly for the other term. Usually, the behaviour of $\langle r^2(t)\rangle$ is similar to what is depicted in figure 6. However, MCT predictions of $\alpha_2(t)$ are quite inaccurate. In general, MCT fails to accurately depict properties such as the non-Gaussian parameter and the breakdown of the Stokes–Einstein relation.

14

One may take from this last result that MCT is not capable of saying anything about dynamically heterogeneous motion in supercooled liquids [12], but perhaps this statement is too strong. We will explore this further in the next section.

2.3. Field-theoretic description

Before finishing this section, we provide a sketch of the field-theoretic approach to schematic MCT [10, 11]. In some sense, the memory function approach can be thought of as arising from coupled Langevin equations for the modes $\delta\rho_{\mathbf{q}}$ and $j_{\mathbf{q}}^{L}$. For example,

$$\delta\dot{\rho}_{\mathbf{q}} = iq j_{\mathbf{q}}^{L}(t), \tag{64}$$

$$\frac{\partial}{\partial t} j_{\mathbf{q}}^{L}(t) = -\frac{iq k_{\mathrm{B}}T}{mS(q)}\delta\rho_{\mathbf{q}}(t) - \frac{k_{\mathrm{B}}T}{m}\int d\mathbf{k}\ \underbrace{(i\hat{\mathbf{q}}\cdot\mathbf{k})c(k)\delta\rho_{\mathbf{q}-\mathbf{k}}(t)\delta\rho_{\mathbf{k}}(t)}_{\text{from the fluctuating force}}$$

$$- \underbrace{\frac{\zeta_0}{m}j_{\mathbf{q}}^{L}(t)}_{\text{viscosity term}} + \underbrace{\eta_{\mathbf{q}}(t)}_{\text{noise term}}. \tag{65}$$

As a toy model for this (forgetting vector labels and wavevectors), we get

$$\dot{\phi}(t) = -\mu(t)\phi(t) - \frac{g}{2}\phi(t)^2 + \eta(t) \tag{66}$$

with $\langle\eta(t)\eta(0)\rangle = 2T\delta(t)$. We also define

$$G_0(t,t') \equiv \exp\left(-\int_{t'}^{t} d\tilde{t}\,\mu(\tilde{t})\right) \tag{67}$$

and

$$(G\bigotimes f)(t) \equiv \int_{0}^{t} dt'\,G_0(t,t')f(t'), \tag{68}$$

where G_0 is the *bare* response function, or propagator. It must be zero if $t < t'$. The solution for $\phi(t)$, with $\phi(0) = 0$ is, in graphical terms,

$$\phi(t) = \longrightarrow\!\!\times + \underset{\frac{g}{2}}{\longrightarrow}\!\!\times + \underset{\frac{g}{2}}{\longrightarrow}\underset{\frac{g}{2}}{\times} + \cdots, \tag{69}$$

where an arrow represents G_0, a $\times$ represents the noise, and a factor of $g/2$ is associated with each branching point. These terms are simply obtained as a solution from integrating equation (66). In a more compact notation,

$$\phi(t) = G_0\bigotimes\eta - \frac{g}{2}G_0\bigotimes\left\{G_0\bigotimes\eta\cdot G_0\bigotimes\eta\right\} + \cdots, \tag{70}$$

where '$\cdot$' is a simple product.

We define two kinds of functions,

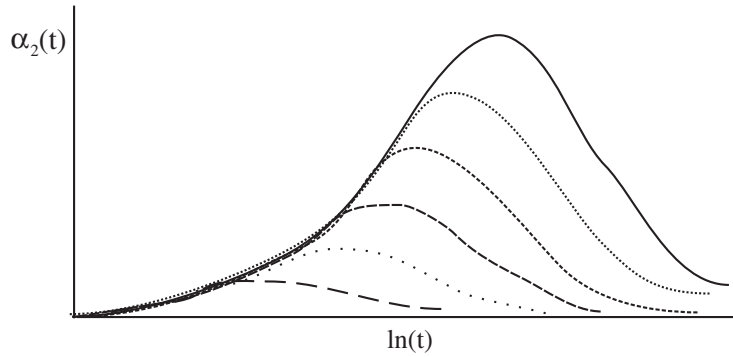$$C(t,t') \equiv \langle\phi(t)\phi(t')\rangle \tag{71}$$

Figure 6. The non-Gaussian parameter as depicted here is one of the features that MCT cannot reproduce accurately. The curves increase in magnitude and spread with decreasing temperature (from left to right).

and

$$G(t,t') \equiv \left\langle \frac{\partial \phi(t)}{\partial \eta(t')} \right\rangle = \frac{1}{2T} \langle \phi(t)\eta(t') \rangle, \tag{72}$$

where the last equality is true for Gaussian noise. Again, $C(t,t')$ can be defined on the entire (t,t') plane but $G(t,t')$ only for $t > t'$. Let us construct a series for the two functions. The zeroth-order contribution to $C(t,t')$ is given as follows:

$$\langle \rightarrow\!\!\times \quad \times\!\!\leftarrow \rangle = \left\langle \int_0^t dt_1\, G_0(t,t_1)f(t_1) \int_0^{t'} dt_2\, G_0(t',t_2)f(t_2) \right\rangle,$$

$$= \int_0^t \int_0^{t'} dt_1\, dt_2\, G_0(t,t_1)G_0(t',t_2)2T\delta(t_1 - t_2). \tag{73}$$

The bracket average implies connecting the $\times$-vertices to form diagrams with none of these left. Diagrams that do not pair up all noise vertices (i.e. those with an odd number of $\times$-vertices) average to zero.

Going beyond zeroth order, we get the following:

$$C(t,t') = \rightarrow\!\!\times\!\!\rightarrow + \left\langle \rightarrow\!\!\bullet\!\!\diamond\!\!\bullet\!\!\leftarrow \right\rangle + \cdots$$

$$= \rightarrow\!\!\times\!\!\rightarrow + \rightarrow\!\!\bullet\!\!\bigcirc\!\!\bullet\!\!\leftarrow + \cdots,$$

$$\equiv \int_0^t dt_1 \int_0^{t'} dt_2\, G_0(t,t_1)D(t_1,t_2)G_0(t',t_2), \tag{74}$$

where to obtain the last line we defined

$$D(t_1,t_2) \equiv 2T\delta(t_1 - t_2) + \frac{g^2}{2}C_0(t_1,t_2)C_0(t_1,t_2) + \cdots. \tag{75}$$

What about $G(t,t')$?

$$G(t,t') = \rightarrow + \left\langle \frac{1}{2T} \rightarrow\!\!\bullet\!\!\!\!<\!\!\times \right\rangle + \cdots, \tag{76}$$
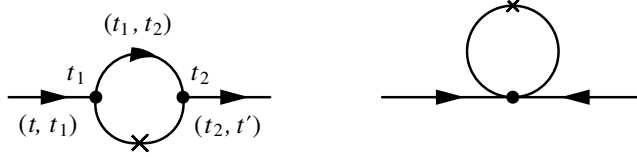
Figure 7. Left: as an exercise, work out the integration limits for this sample diagram. The time pairings indicate the beginning and end times of a given segment. There are in this diagram two internal vertices, t_1 and t_2, and two external ones, t and t'. Right: a simple tadpole diagram.

where the lone $\times$ has to be attached to a $\times$ on the tree and then the remaining diagram is closed. Thus,

$$G(t,t') = \longrightarrow + \longrightarrow\!\!\!\bigcirc\!\!\!\longrightarrow + \cdots,$$

$$= G_0(t,t') + \int_{t'}^{t} dt_1 \int_{t'}^{t_1} dt_2\, G_0(t,t_1)\Sigma(t_1,t_2)G_0(t_2,t'), \tag{77}$$

where we similarly defined

$$\Sigma(t_1,t_2) \equiv g^2 C_0(t_1,t_2)G_0(t_1,t_2) + \cdots. \tag{78}$$

This is an exact, formal representation of the perturbations series. In fact, in some sense it is simply a definition of the kernels D and Σ. We can appeal to the structure of the perturbation series to justify this.

Also, the lower limit of the second integration ensures that $t_2 > t'$. In fact, let us take a closer look at the limits of integration for a sample diagram, the second term in equation (77), which is reproduced on the left-hand side of figure 7 with additional labels. The incoming branch imposes $t > t_1$, the central loop $t_1 > t_2$, and the outgoing branch $t_2 > t'$, for an overall $t > t_1 > t_2 > t'$. The resulting integration limits are thus $\int_{t'}^{t} dt_1 \int_{t'}^{t_1} dt_2$.

If you have followed so far, you might be asking yourself what happened to the diagrams like the one appearing on the right in figure 7. Such closed loops are called *tadpoles*. They do not contribute to the time dependence of C or G, and we assume that their contribution is absorbed into $\mu(t)$. The next lowest order terms are then the diagrammatic forms we last drew in equations (74) and (77).

To make a self-consistent approximation we replace G_0 and C_0 in our second-order approximations for D and Σ by G and C. We will call this the *mode-coupling approximation*, a name that will be clear in meaning at the end [10, 11]. This is equations (74) and (77) with

$$\Sigma(t_1,t_2) = g^2 C(t_1,t_2)G(t_1,t_2), \tag{79}$$

$$D(t_1,t_2) = 2T\delta(t_1,t_2) + \frac{g^2}{2}C(t_1,t_2)^2. \tag{80}$$

These two equations can be further manipulated by noting that

$$G_0 = \left(\mu(t) + \frac{\partial}{\partial t}\right)^{-1}, \tag{81}$$

and so we can multiply both sides of equations (74) and (77) by G_0^{-1}:

$$G_0^{-1} \bigotimes G = I + \Sigma \bigotimes G, \tag{82}$$

$$G_0^{-1} \bigotimes C = G_0^{-1} \bigotimes \left\{ G_0 + G_0 \bigotimes \Sigma \bigotimes G \right\} \bigotimes D \bigotimes G,$$

$$= D \bigotimes G + \Sigma \bigotimes \underbrace{\left\{ G \bigotimes D \bigotimes G \right\}}_{C},$$

$$= D \bigotimes G + \Sigma \bigotimes C, \tag{83}$$

where I is the identity operator. In other notation,

$$\left\{ \frac{\partial}{\partial t} + \mu(t) \right\} G(t, t') = \delta(t - t') + \int_{t'}^{t} \mathrm{d}t'' \, \Sigma(t, t'') G(t'', t'), \tag{84}$$

$$\left\{ \frac{\partial}{\partial t} + \mu(t) \right\} C(t, t') = \int_{0}^{t} \mathrm{d}t'' \, D(t, t'') G(t', t'') + \int_{0}^{t} \mathrm{d}t'' \, \Sigma(t, t'') C(t'', t'). \tag{85}$$

This still does not look like the MCT equations derived before. We will manipulate the RHS of the second equation to achieve this. Taking the first term, we make the substitution

$$\int_{0}^{t} \mathrm{d}t'' \, D(t, t'') G(t', t'') \rightarrow \int_{0}^{t'} D(t, t'') \frac{1}{T} \frac{\partial}{\partial t''} C(t', t''). \tag{86}$$

We can replace $t \rightarrow t'$ because of the restriction on time arguments in $G(t', t'')$ and we can substitute G for C as written by using the *fluctuation-dissipation theorem* (FDT) and assuming that the system is at equilibrium. The result can now be integrated by parts,

$$\frac{1}{T} [D'(t, t'') C(t'', t')]|_0^{t'} - \frac{1}{T} \int_0^{t'} \mathrm{d}t'' \, \frac{\partial}{\partial t''} D'(t, t'') C(t'', t'). \tag{87}$$

Note that we can neglect the δ-function part of D here, since it provides no contribution. So, we denote the regular part of D as D'.

Again, using the FDT, we can make the substitution

$$\frac{\partial}{\partial t''} D'(t, t'') \rightarrow T\Sigma(t, t''), \tag{88}$$

yielding an integral which can be combined with the other term of equation (85) to obtain

$$-\int_0^{t'} \mathrm{d}t'' \, \Sigma(t, t'') C(t'', t') + \int_0^t \mathrm{d}t'' \, \Sigma(t, t'') C(t'', t') = \int_{t'}^t \mathrm{d}t'' \, \Sigma(t, t'') C(t'', t'). \tag{89}$$

Now, using the FDT in the reverse direction and integrating by parts, we get

$$\frac{1}{T} [D'(t, t'') C(t'', t')]|_{t'}^{t} - \frac{1}{T} \int_{t'}^{t} \mathrm{d}t'' \, D'(t, t'') \frac{\partial}{\partial t''} C(t'', t'). \tag{90}$$

Combining all terms on the right-hand side of equation (85), we get

$$\frac{1}{T} [D'(t, t) C(t, t') - D'(t, 0) C(0, t')] - \frac{1}{T} \int_{t'}^{t} \mathrm{d}t'' \, D'(t, t'') \frac{\partial}{\partial t''} C(t'', t'). \tag{91}$$

Using the fact that, in equilibrium, these functions are time-translation invariant,

$$
\begin{aligned}
D'(t, t'') &= D'(t - t''), \\
C(t, t') &= C(t - t'), \\
C(t'', t') &= C(t'' - t'), \\
C(0, t') &= C(t'), \\
D'(t, 0) &= D'(t), \\
D'(t, t) &= D'(0),
\end{aligned}
\tag{92}
$$

and making the transformation,

$$
\begin{aligned}
t'' - t' &\equiv \tau', \\
t - t' &\equiv \tau, \\
t' &\to \infty,
\end{aligned}
\tag{93}
$$

we find

$$
\left(\frac{\partial}{\partial t} + \tilde{\mu}(t) \right) C(t) + \frac{1}{T} \int_0^t \mathrm{d}\tau\, D'(t - \tau) \frac{\partial C(\tau)}{\partial \tau} = 0,
\tag{94}
$$

where

$$
\tilde{\mu}(t) = \mu(t) - \frac{1}{T} D'(0),
\tag{95}
$$

$$
D'(t) = \frac{g^2}{2} C(t - \tau)^2.
\tag{96}
$$

This is just the schematic model with

$$
\Omega_0^2 \leftrightarrow \tilde{\mu}(t),
\tag{97}
$$

$$
\lambda \leftrightarrow \frac{g^2}{2T}.
\tag{98}
$$

The only difference is that $\partial C(t)/\partial t$ appears instead of $\partial^2 \Phi(t)/\partial t^2$. This actually makes *no* difference as far as the glassy properties are concerned. In fact, for models of overdamped systems, such as Brownian colloidal spheres, $\partial \Phi(t)/\partial t$ is what appears naturally in the reduction of the full MCT equations of the schematic model. This completes the relationship between the memory function/projection operator MCT derivation and a field-theoretic approach.

3. Looking ahead: beyond 'simple' MCT

In this section we will outline some thoughts on attempts to do better than the MCT derived thus far. This is not an exhaustive discussion, but is meant to give an idea about what can be done.

3.1. Coupling to currents

Götze and Sjögren [13] as well as Das and Mazenko [14] have developed theories that remove the sharp transition at $T = T_0$. In both cases, it is the couplings to certain current modes that are ignored in the expressions we have just derived that restore ergodicity below T_c.

In the theory of Götze and Sjögren, the Laplace transform of our exact equation of motion for $F(k, t)$ is given as

$$F(k, z) = \frac{-1}{z - \Omega(k)^2/(z + M(k, z))}, \tag{99}$$

where $\Omega(k) = k^2 k_B T/m S(k)$ and $M(k, z)$ is the Laplace transform of the memory function

$$M(k, z) = \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-zt} M(k, t), \tag{100}$$

and, similarly,

$$F(k, z) = \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-zt} F(k, t). \tag{101}$$

Essentially, within the 'extended' MCT of Götze and Sjögren,

$$M(k, z) \sim \frac{K(k, z)}{1 - \delta_h(k, z) K(k, z)}, \tag{102}$$

where $K(k, z)$ is the ordinary MCT memory function given in equation (39). The expression for $\delta_h(k, z)$ is complicated, but to see what it does, note that:

(1) If $\delta_h = 0$, we recover exactly the ordinary MCT that we have derived before. This can be checked by applying a Laplace transform the old expressions.

(2) If $\delta_h(k, z)$ has no singularities as $z \to 0$, the strict transition at T_c in the MCT that we have previously derived is removed since relaxation is governed by $M \sim 1/|\delta_h|$ at long times and not $K(k, z)$, which yields a pole singularity in z space.

In the theory of Das and Mazenko, a hydrodynamic approach is used. The kinetic energy of the free energy functional in terms of current j and density ρ has the form

$$\mathrm{KE}[j, \rho] \sim \frac{j^2}{\rho}. \tag{103}$$

This is like the usual $p^2/2m$ kinetic energy. However, the $1/\rho$ part coupled to the current rounds off the strict singularity at T_c, like in the Götze and Sjögren theory.

Note that in both theories, we need currents to restore ergodicity. For some systems, like (simulated) colloidal hard spheres undergoing Brownian motions, these currents do not exist! Thus, the Götze and Sjögren and the Das and Mazenko theories cannot be used to improve ordinary MCT there.

3.2. New closures

As mentioned above, the extended MCT of Götze and Sjögren and of Das and Mazenko cannot tell us anything (beyond ordinary MCT) for Brownian hard sphere systems. An interesting proposal was recently put forward by Szamel [15]. The main idea is *not* to factorize the memory function expression leading to the ordinary MCT given in equation (39), but to write an *exact* equation of motion for it, and then factorize the memory function for the new equation. Here is a sketch of the idea.

Recall our old approach to MCT,

$$\frac{\partial^2 F(k,t)}{\partial t^2} + \frac{k^2 k_{\mathrm{B}} T}{m S(k)} F(k,t) + \int_0^t \mathrm{d}\tau\, K(k, t-\tau) \frac{\partial F(k,z)}{\partial \tau} = 0, \tag{104}$$

where essentially $K(k,t) \sim \langle \delta\rho\delta\rho\delta\rho\delta\rho \rangle$ is a four-point function of density variables. In the old approach, the closure involved

$$K(k,t) \sim \langle \delta\rho\delta\rho \rangle \langle \delta\rho\delta\rho \rangle = \sum_{\mathbf{q}} F(q,t) F(|\mathbf{k}-\mathbf{q}|, t) \tag{105}$$

and this allowed us to solve for $F(k,t)$.

Instead of factorizing the four-point memory kernel, let us write an exact equation of motion for it, following the same lines of reasoning as before:

$$\frac{\partial^2 K(t)}{\partial t^2} + \Gamma K(t) + \int_0^t \mathrm{d}\tau\, R(t-\tau) \frac{\partial K(\tau)}{\partial \tau} = 0. \tag{106}$$

The wavevector indices are suppressed to simplify the notation in order to clarify the idea behind the manipulations. This has the same form as before, but with new frequencies Γ and a new memory function $R(t-\tau)$.

Schematically, $R \sim \langle \delta\rho\delta\rho\delta\rho\delta\rho\delta\rho\delta\rho \rangle$ is a six-point function! We can close the equation for K and F, by making the approximation $R \approx K \cdot F$, the product of a four-point and a two-point function. This yields two coupled sets of integro-differential equations that may be solved self-consistently yielding a converged $F(k,t)$.

This approach has not been considered for the full dynamics of $F(k,t)$, but yields a better estimate for T_{c} (i.e. the T_{c} that is extracted is closer to the measured glass transition).

3.3. Four-point correlations and dynamical heterogeneities

It was mentioned in section 2 that MCT does not describe well

$$\alpha_2(t) \equiv \frac{3\langle r^4(t) \rangle}{5\langle r^2(t) \rangle^2} - 1 \tag{107}$$

and that $\alpha_2(t)$ seems to correlate well with the timescale of maximal dynamical heterogeneity [16, 17]. It turns out that this timescale is in the late β-regime. This highlights the fact $\alpha_2(t)$ yields information on transiently mobile particles that jump due to the destruction of cages. It should be noted that there is no length scale dependence in $\alpha_2(t)$.

To gain some information about a growing (dynamical) length scale, a multi-point dynamical generalization of the static structure factor may be studied [18]–[21]. The
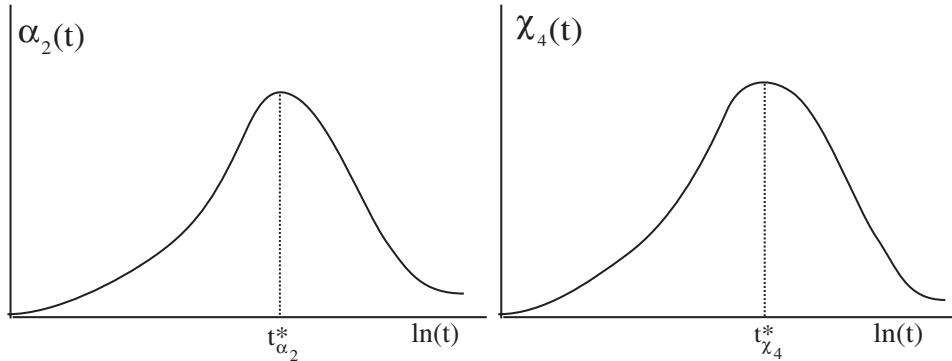
Figure 8. The non-Gaussian parameter $\alpha_2(t)$ (left) and the four-point correlation function $\chi_4(t)$ (right) peak at times t^* where $t^*_{\chi_4} > t^*_{\alpha_2}$.

$k \to 0$ limit of this structure factor, as Sharon Glotzer discusses in her lectures, is the susceptibility

$$\chi_4(t) \sim \int d\mathbf{r}_1 \ldots d\mathbf{r}_4 \, \theta_a(|\mathbf{r}_1 - \mathbf{r}_2|)\theta_a(|\mathbf{r}_3 - \mathbf{r}_4|)$$
$$\times \, \langle \rho(\mathbf{r}_1, 0)\rho(\mathbf{r}_2, t)\rho(\mathbf{r}_3, 0)\rho(\mathbf{r}_4, t)\rangle, \tag{108}$$

where the function $\theta_a(|\mathbf{r}_1 - \mathbf{r}_2|)$ equals one when $|\mathbf{r}_1 - \mathbf{r}_2| \leq a$, and zero otherwise [18]. The timescale at which $\chi_4(t)$ peaks is generally in the α-regime. The growing length scale associated with dynamic heterogeneity is associated with slow moving, transiently caged particles.

Given the superficial similarity with $\alpha_2(t)$, as shown in figure 8, one might conclude that MCT cannot compute objects like χ_4, but this is not the case. Recent work by Biroli and Bouchaud [19], motivated by the earlier insight of Franz and Parisi [20] and Kirkpatrick and Thirumalai [21], shows that MCT may make quantitative statements about the scales of length and time associated with dynamical heterogeneity. So far, absolute length scales have not been computed, but dynamical exponents z relating timescales τ and length scales ξ have:

$$\tau \sim \xi^z, \tag{109}$$

where $z = 2\gamma$ and γ is given in equation (59).

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It should also be noted that in the above two references there are some typos that lead to an MCT equation with an incorrect sign. This was corrected in this version of the derivation.

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