(Crystal) Nucleation: The language

Why crystallization requires supercooling

1. Transferring N particles from liquid to crystal yields energy.

\[ \Delta G_{\text{gain}} = \Delta \mu \times N \]

\( \Delta \mu \): "thermodynamic driving force"

N is proportional to the VOLUME of the crystal (i.e. to \( r^3 \))

Why crystallization requires supercooling

1. But it costs energy to make a surface area S.

\[ \Delta G_{\text{cost}} = \gamma \times S \]

\( \gamma \): "surface tension"

S is proportional to the SURFACE of the crystal (i.e. to \( r^2 \))

\[ \Delta G^* = \frac{16 \pi \gamma^3}{3 \rho^2 |\Delta \mu|^2} \]

Nucleation Rate = prefactor \( \exp \left( -\frac{\Delta G^*}{kT} \right) \)
Computing absolute nucleation rates

Crystallization of NaCl from melt

Other example: hard sphere colloids.
Crystal nucleation of hard-sphere colloids

Equilibrium phase behavior:

Nucleation rates

Discrepancy: >20 orders of magnitude.

Experiments

Simulations

Nature

It is, however, not obvious that this effect is large enough to account for the apparent

density. It has its freezing point at

\[ \epsilon \]

reduced (and can possibly even become non-monotonic) if, as we expect,

different effective Yukawa potentials.

In fact, recent experiments by Sch et al. [16] report that the nucleation rate barely varies with volume fraction. This observation is hard to reconcile with the behaviour of any of the Yukawa models computed rates (Gasser et al. 2006).

In figure 9, we show a comparison of the nucleation rates reported in [16] with the simulation results for those values of \( \kappa \).

The discrepancy between experiment and simulation results suggests that it is incorrect to assume that the same phenomenon occurs in both hard-sphere systems and that the colloidal particles used in these experiments do not have a freezing point near

\[ \eta \]

for

\[ \eta \] = 5.

Conversely, if we choose \( \eta = 5 \), then the observed freezing density can be reproduced by choosing

\[ \kappa \] = 3.33333 for FCC.

This information we obtain directly from our numerical results for the system with the hydrodynamic interactions taken into account, if

\[ \eta - 6 \]

\[ \beta \] = \[ kT/\sigma \]

Longer ranged repulsion

In figure (and from the numbers collected in table 2), different values of \( \kappa \) were used to map onto a Yukawa model with density-strength and range of repulsion (lower \( \gamma \)).

Nucleation Rate depends strongly on strength and range of repulsion (lower \( \gamma \)).

This can be remedied by using the solution suggested by Medina-Noyola [30]. In this approach, doing this, we neglected the hydrodynamic interactions between the colloids. This drawback can be remedied by using the solution suggested by Medina-Noyola [30]. In this approach, doing this, we neglected the hydrodynamic interactions between the colloids.
But – of course - crystal nucleation is HETEROGENEOUS…

Effect of a flat wall on nucleation:

\[ \cos(\theta) = \left( \gamma_{wl} - \gamma_{ws} \right)/\gamma_s \]

CNT:

\[ \Delta G^* = \frac{16\pi}{3} \frac{\gamma_s^3 f(\theta)}{(\rho_s \Delta \mu)^2} \]

with:

\[ f(\theta) = \left( 2 + \cos(\theta) \right) \left( 1 - \cos(\theta) \right)^2 / 4 \]

The effect of surface free energy:

\[ \Delta G^* = \frac{16\pi \gamma_s^3}{3\rho_s^2 |\Delta \mu|^2} \]

Observation: \( \gamma_{\text{Solid-Liquid}} \)

is about one order of magnitude smaller than

\( \gamma_{\text{Solid-Vapour}} \)

Flat wall speeds up nucleation by a factor \( 10^{570} \)

That is why homogeneous nucleation is the exception.
Therefore:

this is easier than this

Consequence:
‘two-step’ nucleation is plausible

Seeded nucleation?
Seeded Crystallization

If the crystal fits well on the template, it is easy to nucleate... however:

RANDOM (!) SUBSTRATES CAN ACT AS UNIVERSAL NUCLEATION SEEDS
(Experiments: Naomi Chayen, Imperial College)

Explanation (Richard Sear)
“For every Cinderella there is a shoe that fits…”

Theory: Richard Sear

D. Frenkel, NATURE, 443, 641, 2006
But this is not the whole story.

Liquid may form a wetting layer

Study crystal nucleation in a regime where the bulk liquid is not even metastable

In this regime, the dense liquid may wet walls

Wetting layer in “large” pore

\[ \Delta G = (\gamma_{11} + \gamma_{1e} - \gamma_{se})f(h) + \rho_l h \Delta \mu \]

\( h < 0 \) \quad \text{and} \quad h > 0 \]
In this regime, the dense liquid may wet walls

Capillary condensation in “small” pore

Which illustrates that:

this is easier than this

Beyond Newtonian dynamics:

1. Langevin dynamics
2. Brownian dynamics
3. Stokesian dynamics
4. Dissipative particle dynamics
5. Stochastic rotation/multi-particle collision dynamics
6. Lattice Boltzmann
7. Etc. etc.

Disordered substrate yields perfect crystal that nucleates in wetting layer ...
These algorithms are often used to simulate molecular motion in a viscous medium, without solving the equations of motion for the solvent particles.

First, consider motion with friction alone:

\[ m \ddot{v} = -\gamma \dot{v}(t') - \nabla U, \]

After a short while, all particles will stop moving, due to the friction.

Better:

\[ m \ddot{v} = -\gamma \dot{v}(t') - \nabla U + \zeta(t), \]

There is a relation between the correlation function of the random force and the friction coefficient:

\[ < \zeta_x(0) \zeta_x(t) > = 2kT \gamma \delta(t) \]

The derivation is straightforward, but beyond the scope of this lecture. The KEY point is that the friction force and the random force ARE RELATED.

\[ < \zeta(0), \zeta(t) > = m < \dot{v}(0)^2 > 2 \gamma \delta(t) = 6kT \gamma \delta(t) \]
Generalized Langevin Equation

Laplace transform

Fluctuation-Dissipation

Limiting case of Langevin dynamics:

No inertial effects ($m=0$)

\[
m \dot{\theta} = -\gamma \ddot{v}(t') - \nabla U + \tilde{\zeta}(t),
\]

Becomes:

\[
0 = -\gamma \ddot{v}(t') - \nabla U + \tilde{\zeta}(t),
\]

“Brownian Dynamics”

(But still the friction force and the random force are related)

What is missing in Langevin dynamics and Brownian dynamics?

1. Momentum conservation
2. Hydrodynamics

(1 implies 2).

Is this serious?

Not always: it depends on the time scales.
Momentum “diffuses” away in a time $L^2/\nu$. After that time, a “Brownian” picture is OK.

However: hydrodynamics makes that the friction constant depends on the positions of all particles (and so do the random forces…).
Momentum conserving, coarse-grained schemes:

Dissipative particle dynamics
Stochastic Rotation Dynamics/Multi-particle collision dynamics
Lattice-Boltzmann simulations

These schemes represent the solvent explicitly (i.e. as particles), but in a highly simplified way.

Outline:
1. Recursive enumeration
   a) Polymer statistics (simulation)
   b) ..
2. Molecular Motors (experiments!)
   (well, actually, simulated experiments)
Consider a lattice (e.g. 2D-square).

At a given point $x_i$, the potential energy is $U(x_i)$.

The Boltzmann factor for a particle at point $x_i$ is 
\[ \exp(-\beta U(x_i)) \equiv z_i^1 \]

The partition function for a single point particle is 
\[ Z_1 \equiv \sum_i z_i^1 \]

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**Dimers**

The Boltzmann factor for a dimer on points $x_i$ and $x_{i+1}$ is 
\[ \exp(-\beta(U(x_i) + U(x_{i+1}))) = z_i^1 \times z_{i+1}^1 \]

The Boltzmann factor for all dimers terminating on point $x_i$ is 
\[ z_i^{(2)} \equiv z_i^1 \times \sum_{j \neq x_i} z_j^1 \]

The partition function for a single dimer is 
\[ Z_2 \equiv \sum_i z_i^{(2)} \]
This method is exact for non-self-avoiding, non-interacting lattice polymers.

It can be used to speed up MC sampling of (self)interacting polymers
B. Bozorgui and DF, Phys. Rev. E 75, 036708 (2007))

NOTE: 'MFOLD' also uses recursive sampling to predict RNA secondary structures.
Experimentally, the step size is measured by fitting the (noisy) data.

Example: noisy “synthetic data”

Best practice: “fit steps to data”

How well does it perform?

1. It can be used if the noise is less than 60% of the step size.
2. It yields a distribution of step sizes (even if the underlying process has only one step size)

Observation:

We want to know the step size and the step frequency but...

We do not care which trace is the “correct” trace.

Bayesian approach: compute the partition function $Q$ of non-reversing polymer in a rough potential energy landscape

As shown before: we can enumerate $Q$ exactly (and cheaply).

From $Q$ we can compute a “free energy”

$$F = -\ln Q$$
Compute the “excess free energy” with respect to reference data

What have we learned?

1. What is Soft Matter?
Soft Matter

Airport security measures
Prepare for security

If you have any of these items, you must return to Check-in or dispose of them safely.

Any items purchased after Security can be taken on board. Special restrictions may apply to items taken on flights to the USA.

Time to stop!

REBOOT
UNIVERSE