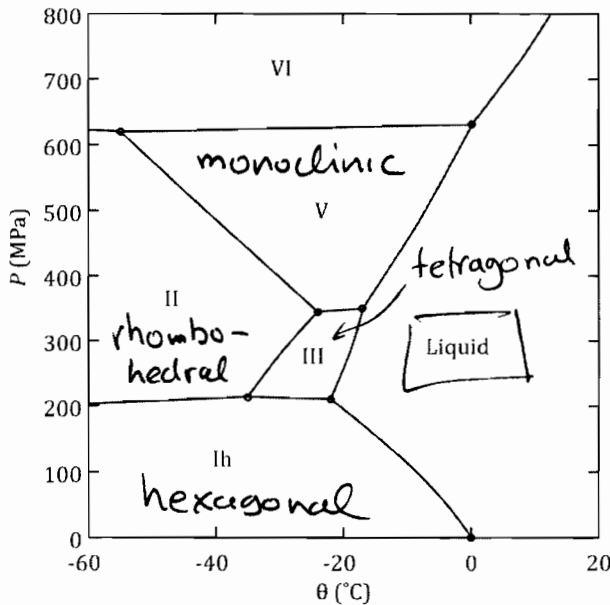


Polymorphism

Solids can have different crystal structures, depending on T and P . For example, many possible phases of H_2O are known as shown here.



←

Knowing which phase is thermodynamically stable at given conditions can be very important!

Famous example: Ritonavir (antiviral) the form approved was a metastable solid - the stable solid is inactive (does not dissolve). Once some stable solid was made from a minor change in production conditions, it was very hard to get back the active form!

→ need free energy calculations of different crystal structures

Interfacial simulations between 2 solids do not work because there are large barriers to crystal structure transformations - simulations show huge hysteresis

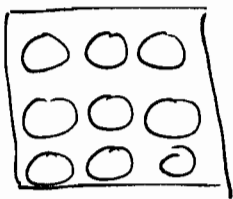
Approach: ① Construct reversible path from hypothesized crystal structure to a state of known free energy

② Repeat for other structures (or the liquid)

③ Find the (T, P) points of coexistence:

$$T_I = T_{II} \quad P_I = P_{II} \quad \mu_I = \mu_{II} \quad (I, II: \text{coexisting phases})$$

Frenkel-Ladd approach (J. Chem. Phys. 81: 3188 (1984)]
for atomic solids: reversibly transform crystal into Einstein (harmonic) solid



real crystal
 $U_0(\vec{r}^N)$

parameter
 λ



Einstein crystal
 $U_E = \sum_{i=1}^N k_i (\vec{r}_i - \vec{r}_{i,0})^2$

$$U = (1-\lambda)U_0 + \lambda U_E$$

$$A = \underbrace{A_{\text{Einstein solid}}}_{\text{known theoretically}} + \int_0^1 d\lambda \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_{\lambda} =$$

$$= A_{\text{Einstein solid}} + \int_0^1 d\lambda \left\langle \sum_{i=1}^N k_i (\vec{r}_i - \vec{r}_{i,0})^2 - U_0(\vec{r}^N) \right\rangle$$

How do we select the spring constants k_i ?

→ too stiff (high) or too soft result in harder / less accurate integrations over Δ

Optimal selection when the mean-squared-displacements of atoms from their equilibrium positions are similar in the real + Einstein crystals:

$$\left\langle \sum_{i=1}^N (\vec{r}_i - \vec{r}_{i,0})^2 \right\rangle_{\Delta=0} = \left\langle \sum_{i=1}^N (\vec{r}_i - \vec{r}_{i,0})^2 \right\rangle_{\Delta=1}$$

Using the known result for harmonic motions

$$\frac{3k_B T}{2k_i} = \left\langle (\vec{r}_i - \vec{r}_{i,0})^2 \right\rangle_{\Delta=0}$$

Fixing the Center-of-mass

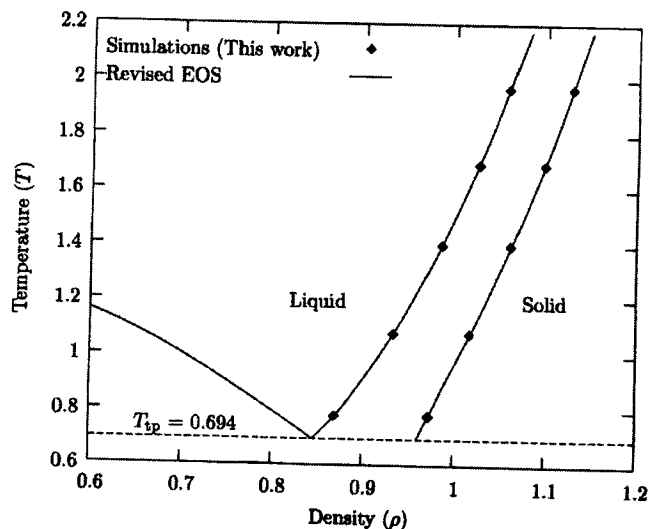
When the springs are on, the crystal as a whole cannot move; for $\Delta=0$, however, there is no such constraint, resulting in very large values of the integrand at low Δ

- Solution:
- fix center-of-mass of crystal by moving all ^{other} particles in opposite direction when a particle is displaced in Monte Carlo
 - do not "put back" particles in periodic box

Example - LJ melting Curve

Mastny + de Pablo J. Chem. Phys. 127(2007)

104504-7 Melting line of the Lennard-Jones system



104504-5 Melting line of the Lennard-Jones system

J. Chem. Phys. 127, 104504 (2007)

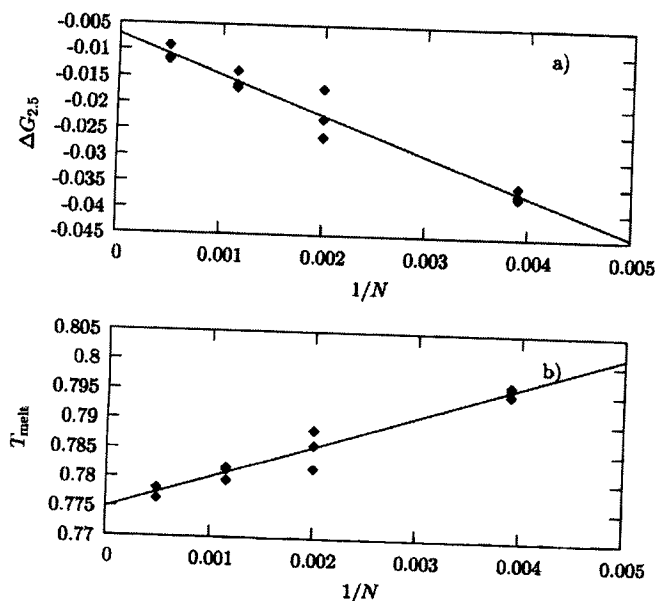


FIG. 1. The linear scaling dependence of thermodynamics properties. Individual simulation results are shown (symbols) along with best fit lines. (a) shows the $1/N$ scaling of solid-liquid relative Gibbs free energy at $T=0.77$ and $P=1.0$. (b) shows the $1/N$ scaling of the melting temperature at $P=1.0$.

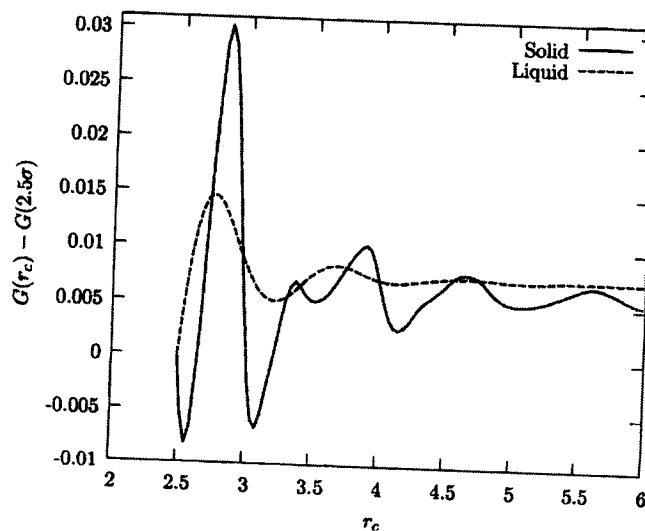
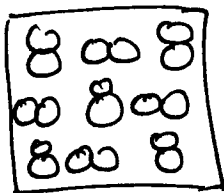


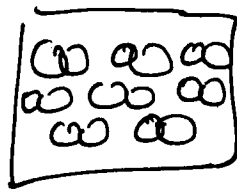
FIG. 2. The Gibbs free energy of both the solid and liquid phases as function of the cutoff radius, at $T=0.77$ and $P=1.0$. The free energy of each phase is referenced to the phase free energy with $r_c=2.5$.

Molecular Solids

The approach above may not work for molecular solids because of phase transformations at some value of λ due to orientations:



Phase I



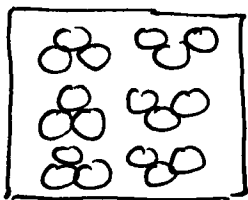
Phase II

(as λ increases, shape of potential becomes less important)

Solution: two-step process [Meijer et al., JCP 92 (1990)]

I. Couple to lattice positions with harmonic springs, but maintain original potential to keep orientations fixed

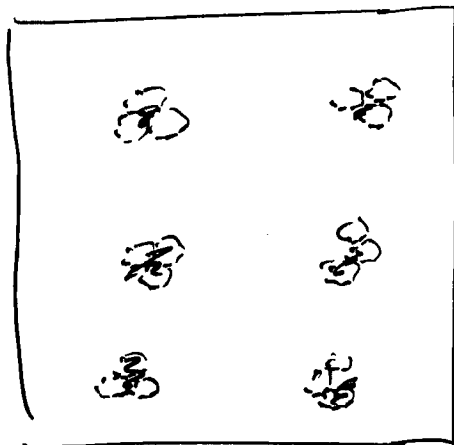
II. Expand to large volume $V \rightarrow \infty$, for which the potential becomes irrelevant



λ



expand



Einstein crystal