Statistical Physics & Condensed Matter Theory I: Exercise

Melting and the Lindemann criterion

You all know that a given crystal will eventually melt upon heating, because of the thermal fluctuations in the positions of the atoms on the lattice. In 1910 (before the advent of quantum mechanics), Lindemann formulated a criterion for melting, based on looking at the thermal fluctuations of atomic positions. His criterion reads

$$\frac{\Delta x^2}{a^2} < c_L, \qquad \Delta x^2 \equiv \langle x^2 \rangle - \langle x \rangle^2$$

where x is the variable representing the position of an atom, Δx^2 is its mean-square fluctuation, a is the lattice spacing, and c_L is a numerical constant, whose value we can expect to be $c_L \simeq 0.1$[1].

We however know that *quantum* fluctuations are present, even at zero temperature. Can quantum mechanics thus melt crystals?

First guess

Let us first look at a single atom. Taking $\hat{x}$ to be its position (deviation from equilibrium) and $\hat{p}$ to be its momentum operator (with the usual canonical commutation relations: $[\hat{x}, \hat{p}] = i\hbar$), we approximate its Hamiltonian as a simple Harmonic oscillator,

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2.$$

Show that the Lindemann criterion then reads

$$\frac{\hbar}{2m\omega a^2} < c_L.$$

Linear chain of atoms

The calculation using an isolated atom is not very credible, since we have neglected all the neighbours (*i.e.* the crystal itself). A much better starting point is our theory of the (quantum) harmonic chain of N atoms with mean interatom spacing a. This was described in terms of variables $\hat{\Phi}_I$ representing the deviation of the Ith atom from its equilibrium position $x_I^0 = Ia$. The Hamiltonian is

$$H = \sum_{I=1}^{N} \frac{\hat{\Pi}_I^2}{2m} + \frac{k_s}{2}(\hat{\Phi}_{I+1} - \hat{\Phi}_I)^2$$

where the position (deviation) $\hat{\Phi}_I$ and momentum $\hat{\Pi}_I$ operators obey the canonical commutation relations

$$\left[\hat{\Phi}_I, \hat{\Pi}_{I'}\right] = i\hbar\delta_{II'}$$

[1] This Lindemann constant can be pictured as follows: if the root-mean-square fluctuations in the position are about one-third of the interatomic distance, the crystal melts. You can thus expect that $c_L \simeq (1/3)^2 \sim 0.1$.

and we impose periodic boundary conditions $\hat{\Phi}_{I+N} = \hat{\Phi}_I$ (similarly for Π_I).

Using the Fourier transforms

$$\hat{\Phi}_I = \frac{1}{\sqrt{N}} \sum_p e^{ipIa} \hat{\Phi}_p, \qquad \hat{\Phi}_p = \frac{1}{\sqrt{N}} \sum_I e^{-ipIa} \hat{\Phi}_I,$$
$$\hat{\Pi}_I = \frac{1}{\sqrt{N}} \sum_p e^{-ipIa} \hat{\Pi}_p, \qquad \hat{\Pi}_p = \frac{1}{\sqrt{N}} \sum_I e^{ipIa} \hat{\Pi}_I,$$

with momenta $p = \frac{2\pi}{Na} n$, $n = -\frac{N}{2} + 1, ..., \frac{N}{2}$ (the canonical commutation relations between momentum modes are then $\left[\hat{\Phi}_p, \hat{\Pi}_{p'}\right] = i\hbar\delta_{pp'}$), show that the Hamiltonian can be rewritten

$$H = \sum_p \frac{\hat{\Pi}_p \hat{\Pi}_{-p}}{2m} + \frac{m\omega_p^2}{2} \hat{\Phi}_p \hat{\Phi}_{-p}, \qquad \text{with} \quad \omega_p = 2\sqrt{\frac{k_s}{m}}\, |\sin(\frac{pa}{2})|.$$

Diagonalization using ladder operators

Define now the ladder operators

$$a_p \equiv \sqrt{\frac{m\omega_p}{2\hbar}} \left(\hat{\Phi}_p + \frac{i}{m\omega_p} \hat{\Pi}_{-p} \right), \qquad a_p^\dagger \equiv \sqrt{\frac{m\omega_p}{2\hbar}} \left(\hat{\Phi}_{-p} - \frac{i}{m\omega_p} \hat{\Pi}_p \right).$$

Show that these obey the canonical commutation relations

$$[a_p, a_{p'}^\dagger] = \delta_{pp'}, \quad [a_p, a_{p'}] = 0, \quad [a_p^\dagger, a_{p'}^\dagger] = 0$$

and that the Hamiltonian can be rewritten as

$$H = \sum_p \hbar\omega_p (a_p^\dagger a_p + \frac{1}{2}).$$

Mean square deviations

Consider now a particular atom of the chain, labeled by I. Show that the mean square deviation of $\hat{\Phi}_I$ in the ground state of the chain is given by

$$\Delta\Phi_I^2 \equiv \langle 0|\hat{\Phi}_I^2|0\rangle - \langle 0|\hat{\Phi}_I|0\rangle^2 = \frac{1}{N} \sum_p \frac{\hbar}{2m\omega_p}.$$

Going to the infinite-length limit $N \to \infty$ and using $\frac{1}{N}\sum_p(...) \to a\int_{-\pi/a}^{\pi/a} \frac{dp}{2\pi}$, argue that in the one-dimensional case, it is impossible to satisfy the Lindemann criterion.

Higher dimensions

Extend your reasoning to the arbitrary-dimensional case (more precisely: give the formula for the mean square deviation). According to the Lindemann criterion, is a crystal at zero temperature possible at all in 2d? In 3d?