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Theoretical Statistical Physics (MKTP1) — Winter term 2020/21

Assignment 7

Handout 18.12.2020 – Return 14./15.01.2020 – Discussion 21./22.01.2020

Exercise 7.1 [5 points]: Including optical phonons in the Debye model

Consider a NaCl crystal that has a diatomic basis and therefore not only acoustic but also optical phonons. In the spirit of the Debye model, the density of states in the phonon spectrum can be approximated as

$$D(\omega) = D_{\mathrm{D}}(\omega) + \delta(\omega - 2\omega_{\mathrm{D}}) \quad \text{with} \quad D_{\mathrm{D}}(\omega) = \begin{cases} 3\frac{\omega^2}{\omega_{\mathrm{D}}^3} & \text{for} \quad \omega \leq \omega_{\mathrm{D}} \\ 0 & \text{for} \quad \omega > \omega_{\mathrm{D}}\,. \end{cases} \tag{1}$$

The first contribution describes the acoustic phonons as discussed in the lecture. The second contribution approximately describes the optical phonons.
Calculate the specific heat of the crystal for high and low temperatures.

Exercise 7.2 [8 points]: Rigid rotator

Consider a molecule, such as carbon monoxide, which consists of two different atoms, one carbon and one oxygen, separated by a distance d. Such a molecule can exist in quantum states of different orbital angular momentum. Each state has the energy

$$\epsilon_l = \frac{\hbar^2}{2I} l(l+1) \tag{2}$$

where $I = \mu d^2$ is the moment of inertia of the molecule about an axis through its centre of mass and μ is the reduced mass defined by $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$. $l = 0, 1, 2, \ldots$ is the quantum number associated with the orbital angular momentum. Each energy level of the rotating molecule has the degeneracy $g_l = 2l + 1$.

1. Find the general expression for the canonical partition function Z. *(1 point)*
2. Show that for high temperatures, Z can be approximated by an integral. Calculate the integral. HINT: For high T, find an approximate integral representation for the summands at given l and demonstrate that the integral can be extended over the complete summation range. *(2 points)*
3. Evaluate the high temperature mean energy E and the heat capacity C_{V}. *(2 points)*
4. Find the low-temperature approximations to the canonical partition function, the mean energy E and the heat capacity C_{V}. *(3 points)*

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Exercise 7.3 [7 points]: Adsorption of molecules to a surface

Consider a gas in contact with a solid surface. The molecules of the gas can adsorb to specific sites on the surface. These sites are sparsely enough distributed over the surface that they do not directly interact. In total, there are N adsorption sites, and each can adsorb $n = 0$, $n = 1$ or $n = 2$ molecules. When an adsorption site is unoccupied, the energy of the site is zero. When an adsorption site is occupied by a single molecule, the energy of the site is ϵ_1. When an adsorption site is doubly occupied, the adsorption energy is ϵ_2. In addition, the two adsorbed molecules can interact in a vibrational mode with frequency ω, so that the energy of the doubly occupied adsorption site is

$$\epsilon_2 + \nu\hbar\omega \quad \text{with} \quad \nu = 0, 1, 2, \ldots . \tag{3}$$

The gas above the surface can be considered as a heat and particle reservoir with temperature T and chemical potential μ.

1. Calculate the grand canonical partition sum Z_{G}. *(2 points)*
2. Calculate the grand canonical potential Ψ. *(1 point)*
3. Calculate the mean number of adsorbed molecules on the surface directly from Z_{G}. *(1 point)*
4. Calculate the mean number of adsorbed molecules on the surface directly from Ψ and convince yourself that it gives the same as calculated in 3. *(2 points)*
5. Give the probability that an adsorption site is in the state with $n = 2$ and $\nu = 3$. *(1 point)*

Exercise 7.4 [10* points]: Random walk and self-avoiding random walk

Write two small computer programs for random walks (RWs) on a 2D square lattice:
- one for the usual random walk, where the walker is allowed to come back to points already visited
- one for the so-called self-avoiding random walk (SAW), where the walker is *not* allowed to do so and hence does not cross its own path.

Show some representative trajectories.
Measure the mean squared displacements (MSD) $\langle x^2(n)\rangle$ as a function of the number of steps n for both cases (the average is over different trajectories). If you plot the results in log-log-scale you can extract the exponents α, where $\langle x^2(n)\rangle \propto n^\alpha$, for the two cases. Compare and discuss.

HINT: One can find a lot of algorithms for the SAW in the web. It is ok to use just the simplest one: When the walker revisits a position, you discard the walk. Otherwise you use the trajectory. Note that this algorithm for the SAW is not very efficient (you have to reject more and more trajectories for larger n), so you should restrict yourself to $n < N$ with, say, $N = 30$. For the usual random walk there is no such problem and you can explore larger N.

* **Bonus points**