Oblig03 — Fys2160 — 2015

Exercise 0.3. Vacancies in a crystal

In this project[1] we will address micro- and macro-states of vacancies in a crystal using the machinery we have developed for the microcanonical ensemble.

In crystalline matter the atoms are organized into a regular pattern — a crystal lattice as shown in Fig. 0.1. When the temperature is zero and the system is in perfect equilibrium all the atoms are in their minimum energy configurations and the lattice is perfectly ordered. However, at finite temperatures the lattice will no longer be perfectly ordered, because thermal fluctuations will introduce imperfections in the lattice. The atoms will oscillate around their average positions (this occurs even at zero temperature), but at finite temperatures the atoms may leave their lattice position and move to a different position. This may leave a vacancy - an empty space in the lattice - formed as an atom leaves its equilibrium position and migrates to the surface of the crystal. We do not here specify the migration mechanisms, but introduce an energy cost $\Delta\varepsilon$ assiciated with the formation of a vacancy: We assume that the energy of the system increases by $\Delta\varepsilon$ when an atom is moved from an interior position to the surface, forming a vacancy in the process.

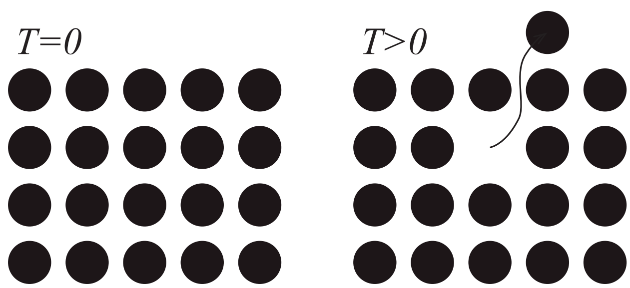

Fig. 0.1 Illustration of a crystal with a vacancy.

a) Find the multiplicity of a crystal with N atoms and n vacancies.

b) Find the entropy $S = S(n,N,V)$.

c) Find an approximation for the entropy without any factorials when $n \ll N$ and $N \gg 1$.

d) What is the temperature of the crystal when it contains n vacancies.

e) Find an expression for the number of vacancies as a function of T. Discuss if this is a fluctuating value in this system.

f) How many vacancies are there in the limit when $T = 0$?

[1] This project is inspired by an exercise developed by Terje Finstad for Fys114.

g) If we assume that $\Delta\varepsilon = 1$eV. Plot the concentration of vacancies as a function of T.

h) Assume that $n \ll N$. Find an expression for the heat capacity as a function of temperature. Plot the heat capacity as a function of temperature from $T = 0$ to $T = 1000$ for this system. Comment.

i) (Discussion question for class discussion): A real crystal will have several contributions to its entropy. Vacacies are one possibility. Interstitial atoms - atoms that occupy places in between the regular lattice spaces - are another. In addition we must include the base vibrations of the crystal. Discuss the contributions of the various effects to the entropy and to the heat capacity of a crystal.

Exercise 0.4. Micro- and Macrostates of a polymer

Polymer materials consists of long molecular strands that can be tangled into a complex configurations with many possible microstates. The entropic contribution to the mechanical properties of polymers are important. In this project we will introduce a simplified model of a polymer to understand how entropy affects mechanical properties of a polymer and how mechanical behavior can affect the thermal state of a polymer.

We will start with a one-dimensional model for a polymer chain. The chain consists of N links of length ΔL corresponding to the basic monomer components of the polymer. The polymer may bend at the "hinges" between the monomer links of length ΔL. In a one-dimensional model, the polymer consists of a sequence of links, where each link can point to the left or to the right. We describe the macro-state of the polymer chain by its net length L.

a) Find an expression for the multiplicity of the macrostate in terms of N and N_R, the number of links pointing to the right.

b) Find how L is related to N and N_R.

c) Find the entropy as a function of L and N.

d) For the one-dimensional system, the work done on the polymer from an external (tension) force F when the polymer is extended a distance dL is $W = FdL$. Show that the thermodynamic identity for this system is $TdS = dE - FdL$.

e) Use the thermodynamic identity to find an expression for the force F as a partial derivative of the entropy. Find the tension F in terms of L, T, N, and ΔL for the system.

f) Show that Hooke's law is valid, that is, when $L \ll N\Delta L$ show that F is proportional to L.

g) Discuss the temperature dependence of F. How does F change if you increase or decrease the temperature? Does this make sense to you?

h) If you hold a relaxed rubber band and suddenly stretch it, would you expect the temperature of the band to increase or decrease? Explain your answer. (You can try this experimentally by placing a rubber band on your tongue and pulling it. Your tongue is quite sensitive to changes in temperature.)