



**Solid State Theory**  
**Problem Set 1 — molecular interactions and crystal structure**

hand-out Wed 13.4., return Wed 20.4.

- 1) **van-der-Waals attraction:** Reconsider the problem of two interacting permanent dipoles. Write down the (classical) partition function at fixed separation  $\mathbf{r}$  and calculate the free energy of interaction within second-order perturbation by summing over all dipole orientations. Obtain the numerical prefactor exactly.
- 2) **polarizability, spontaneous dipole moment:**
  - a) Consider a simple classical model for the polarizability of an atom by assuming the nuclear charge  $+Q$  to be concentrated at a point and the electronic charge  $-Q$  to be smeared out homogeneously over a sphere of radius  $R$ . In a small electric field  $\mathbf{E}$ , calculate the resultant dipole moment  $\mathbf{P}$  and from the definition  $\mathbf{P} = \alpha\mathbf{E}$  the polarizability  $\alpha$ .
  - b) Within the same model, calculate the spontaneous dipole moment  $\langle \mathbf{P}_{sp}^2 \rangle$  by using the equipartition theorem, i.e., by assuming that the internal energy per degree of freedom equals  $k_B T/2$ . Alternatively, you can calculate the expectation value directly by a Gaussian integral. (Hint: Always use the approximation of small amplitudes.)
  - c) With the result for the spontaneous dipole moment, write down the van-der-Waals interaction between two polarizable, non-polar atoms. What is the interaction at contact, i.e. when the atoms just touch? Note that this is a classical calculation, which at low temperatures is replaced by the quantum-mechanical result.
- 3) **van-der-Waals interaction between macroscopic bodies:** Assume two semi-infinite half spaces of matter, at a separation  $D$ . Two volume elements interact via pairwise potentials  $V_{vdw}(\mathbf{r}, \mathbf{r}') = A/(\mathbf{r} - \mathbf{r}')^6$ .
  - a) What is the interaction between the two half spaces as a function of their mutual distance  $D$ ? Note that this energy has units of energy per area. Can one guess the functional dependence on  $D$  without doing a calculation?
  - b) Using your result for the pair potential of two polarizable atoms, what is your estimate for the dimensionless number  $A$ ? What would be your estimate for the interfacial tension, i.e., the energy needed to create one free surface?

- 4) **crystal structures in 2D:** A popular pair potential that incorporates the repulsion between atoms at small distances is the Lennard-Jones potential

$$V_{LJ}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right].$$

Assume interactions only between nearest neighbors and next-nearest neighbors.

- a) Calculate the equilibrium lattice constant and the equilibrium energy per atom,  $U/N$ , in 2D for a square lattice, hexagonal lattice, and for the honey-comb lattice. What is the preferred lattice structure in 2D?
- b) Calculate the bulk compressibility modulus  $B = V\partial^2U/\partial V^2$  where  $V$  is the volume and  $U$  the total crystal energy.
- 5) **packing fraction in 3D:** Assume spheres to pack with maximal density on a face-centered cubic, body-centered cubic, and on a hexagonal lattice. What are the packing fractions of these lattices? Which lattice gives the highest packing fraction?