ETH Zurich
Department of Mechanical and Process Engineering
Statistical Mechanics of Elasticity
Exercise 5 - Summer 2007

Institute for Mechanical Systems
Center of Mechanics
Prof. Dr. Sanjay Govindjee
Felix Hildebrand

Useful Definitions

The canonical partition function

The partition function of a system interacting with a heat bath of temperature T is given by

$$Z(T) = \int_{\Gamma} e^{-\frac{H(\mathbf{q},\mathbf{p})}{k_B T}} \, \mathrm{d}\mathbf{q} \, \mathrm{d}\mathbf{p}, \tag{1}$$

where $H(\mathbf{q},\mathbf{p})$ is the Hamiltonian of the considered system, T the temperature of the surrounding heat bath (in degree Kelvin) and $k_B = 1.38044 \cdot 10^{-23} J/K$.

Free energy

Helmholtz free energy F can be obtained from the partition function using

$$F = -k_B T \ln Z, \tag{2}$$

where k_B is Boltzmann's constant (see above).

Problem 1 - Nonideal monoatomic gas

Derive an approximate expression for the first term of the "virial expansion" for a nonideal gas of N indistinguishable particles in a volume V at low temperature T. The particles interact via a pair potential of the Lennard-Jones form

$$u(r) = u_o \left[\left(\frac{a}{r}\right)^{12} - 2\left(\frac{a}{r}\right)^{6} \right], \tag{3}$$

see Figure 1 for a qualitative representation. Recall that the general virial expansion has the form

$$\frac{\bar{p}}{kT} = n + B_2(T)n^2 + B_3(T)n^3 + \dots \quad . \tag{4}$$

Plot the obtained approximation of the virial coefficient $B_2(T)$.

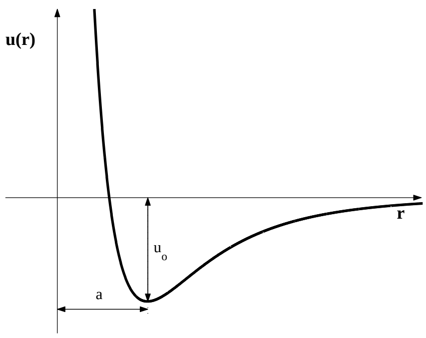

Figure 1: Qualitative plot of the Lennard-Jones potential.

ETH Zurich
Department of Mechanical and Process Engineering
Statistical Mechanics of Elasticity
Exercise 5 - Summer 2007

Institute for Mechanical Systems
Center of Mechanics
Prof. Dr. Sanjay Govindjee
Felix Hildebrand

Homework 1 - Thermal expansion of two particles

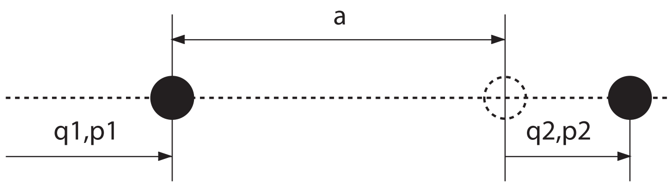

Figure 2: A one-dimensional two-particle system.

Consider a one-dimensional system of two particles with masses m interacting via a Lennard-Jones potential of the form

$$u(r) = u_o \left[\left(\frac{a}{r} \right)^{12} - 2 \left(\frac{a}{r} \right)^{6} \right], \tag{5}$$

where $r = a$ is the location and $u(a) = u_o$ the depth of the energy well corresponding to the spacing at $T = 0K$.

Choose the coordinate systems (q_1, p_1) and (q_2, p_2) such that $q_1 = 0$ and $p_1 = 0$ at all times (this coordinate system moves with the left particle) and $q_2 = 0$ at $q_1 = a$, see Figure 2.

a) Derive the Hamiltonian $H(q_1, p_1, q_2, p_2)$ of this system.

b) Compute the (canonical) partition function of the system. To do so, make use of a Taylor expansion of $u(r)$ about $r = a$ (which is $q_2 = 0$) up to (i) second, (ii) third and (iii) forth order terms. Use equation (7) when adequate to compute the resulting integrals.

c) Compute the expectation value for the separation $\bar{r}(T) = a + \bar{q}_2(T)$. Again, make use of a Taylor expansion of $u(r)$ up to (i) second, (ii) third and (iii) forth order terms and use equation (7) when necessary.

d) Compute the thermal expansion $\alpha(T) = \frac{\bar{r}'(T)}{\bar{r}(T)}$ for (i),(ii) and (iii).

In above calculations, integrals of the form

$$I = \int_{-\infty}^{+\infty} x^n \exp\left(\sum_{i=0}^{N} a_i x^i\right) \mathrm{d}x \tag{6}$$

can be approximated by

$$I \approx \int_{-\infty}^{+\infty} x^n \exp\left(\sum_{i=0}^{2} a_i x^i\right)\left(1 + \sum_{i=3}^{N} a_i x^i\right) \mathrm{d}x. \tag{7}$$

Such integrals can easily be solved using the formulae provided on the last hand out.

All calculations can be carried out by hand, however, you might use Mathematica or Matlab if preferred.

Questions/Comments/Suggestions? Felix Hildebrand - CLA H23.1 - 044/632-7755 - felixhi@ethz.ch