

HW 4: Due October 1

Fluctuations

1. **Small systems:** Let us consider a 1-dimensional harmonic oscillator with a Hamiltonian

$$H(p, x) = \frac{p^2}{2m} + \frac{1}{2}kx^2 \quad (1)$$

where p is the momentum and x is the position. Here, m is the mass and k is the spring constant. If the 1-dimensional oscillator follows the canonical distribution at temperature T ,

- (a) calculate the average energy \bar{H} .
- (b) calculate the relative standard deviation of energy in the ensemble, *i.e.*, calculate $\frac{\sqrt{\Delta H^2}}{\bar{H}}$ (a.k.a. the coefficient of variation), where $\Delta H = H - \bar{H}$.
2. **Large systems:** For 0.01 moles of an ideal gas (~ 2 dl at STP) which is in contact with a heat bath at a temperature T ,

- (a) calculate the average energy \bar{H} .
- (b) calculate the relative standard deviation of energy in the ensemble, *i.e.*, calculate $\frac{\sqrt{\Delta H^2}}{\bar{H}}$.

Can you see any difference between small and large systems in terms of the relative standard deviation of energy in the canonical ensemble?

Remark: The standard deviations from the averages are also called “fluctuations”. These fluctuations are important in the study of phase-transitions, obtaining estimates of continuum quantities like heat capacity, viscosity, thermal conductivity etc.

Heat Capacity

3. The constant-volume heat capacity is given by

$$C_V = \frac{\partial \bar{H}}{\partial T}(V, T) \quad (2)$$

- (a) For an ideal gas consisting of N molecules, calculate the heat capacity using (2).
- (b) In the class, we have seen that heat capacity can be expressed in terms of fluctuations of energy in the canonical ensemble. Use that expression and obtain the expression for heat capacity.

Remark: It is remarkable that a continuum quantity like heat capacity can be expressed in terms of fluctuations of quantities in a statistical ensemble.

4. (Discrete Two Level System) Consider a system that can only be in two energetic states ϵ and $\epsilon + \Delta$. Assume that the system is in thermal equilibrium with a heat bath with absolute temperature T .
- Write down the partition function for this system.
 - What is the mean energy of the system?
 - What is the heat capacity for the system? [$c = dU/dT$]

Thermo-Mechanical Properties

5. (Molecular Thermal Expansion) Two atoms of mass m interact via a Lennard-Jones potential in one-dimension

$$V(x) = V_o \left[\left(\frac{a}{x} \right)^{12} - 2 \left(\frac{a}{x} \right)^6 \right], \quad (3)$$

where $x > 0$ is the separation distance and $V_o \gg kT$ and a are given parameters. Determine the coefficient of thermal expansion for this molecule; i.e. find

$$\alpha = \frac{1}{\bar{x}} \frac{\partial \bar{x}}{\partial T}. \quad (4)$$

Hints:

- The potential energy in this problem is not easy to integrate. A viable strategy is to expand the potential in terms of a Taylor series about its minimum which occurs at $x = a$ with value $-V_o$. Expand out to 4th order terms.
- Choose a coordinate system where the first mass is always $q_1 = 0$ and the second mass' position is given relative to a ; i.e. take $q_2 = x - a$.
- Integrals with exponentiated polynomials in q_2 can be approximated for $kT \ll V_o$ as:

$$\int_{-a}^{\infty} e^{-\sum_{i=0}^N c_i q_2^i} dq_2 \approx \int_{-\infty}^{\infty} e^{-c_0 - c_1 q_2 - c_2 q_2^2} \left(1 - \sum_{i=3}^N c_i q_2^i \right) dq_2. \quad (5)$$

- (d) Recall

$$\frac{d}{d\alpha} \int_{-\infty}^{\infty} e^{-\alpha f(x)} dx = \int_{-\infty}^{\infty} -f(x) e^{-\alpha f(x)} dx \quad (6)$$

- (e) Test: For (solid) Argon (near 0K) $a = 0.376$ nm and $V_o = 167 \times 10^{-16}$ erg. Is your number for α appropriate for a solid?

Remark: This problem shows that simple quadratic energy interactions lead to zero coefficients of thermal expansion. Cubic interactions are needed to get non-zero coefficients of thermal expansion.