PROBLEM SET 7

Reading: Kittel & Kroemer, Ch. 6

When to start which problems?

- Problems 1, 2, 6 and 7 immediately
- Problem 3 after class on Wednesday (Lecture 8A)
- Problems 4, 5, and 8 after Friday (Lecture 8B)

1. *Adsorption.* An adsorption site on the surface of a solid can bind two atoms of a noble gas A. Let $\varepsilon_0 = 0$ be the energy of the site when it is empty, and let $\varepsilon_2 < 0$ be the energy when two atoms of A are attached. Assume that there are no internal degrees of freedom for the complex of two atoms bound to the site, and assume that the energy when a single A atom is attached to the site is so high that this state can be neglected.

   a. Suppose that the chemical potential μ and temperature τ of the gas of atoms are known. What is the probability P_2 that there are two atoms of A bound to the site, at a given moment?

   b. If the site is in equilibrium with a dilute (ideal) gas of A atoms at temperature τ, how does the adsorption probability P_2 depend on the pressure p of atoms in the gas and the temperature τ?

   c. Sketch the adsorption probability P_2

      i. *vs.* pressure p at fixed temperature τ

      ii. *vs.* temperature τ at fixed pressure p

2. *Hemoglobin* (from K&K 5.14). A hemoglobin molecule can bind four O_2 molecules at distinct sites. Assume that ε is the energy of each bound O_2, relative to O_2 at rest at infinite distance. Let $\phi = e^{\beta\mu}$ denote the activity (fugacity) of the free O_2 in solution.

   a. What is the probability that one and only one O_2 is adsorbed on a hemoglobin molecule? Sketch the result qualitatively as a function of ϕ.

   b. What is the probability that four and only four O_2 are adsorbed? Sketch this result also.

3. Kittel & Kroemer Problem 6.2 (*Symmetry of filled and vacant orbitals*).

4. Kittel & Kroemer Problem 6.11 (*Convective isentropic equilibrium of the atmosphere.*)

5. Kittel & Kroemer Problem 6.14 (*Ideal gas calculations.*)

6. *Compressibility and density of states.* Derive a relationship between the isothermal compressibility $\kappa_\tau = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{\tau,N}$ and the *thermodynamic density of states* $\left(\frac{\partial n}{\partial \mu}\right)_\tau$.

   a. First, give a physical interpretation of $(\partial n/\partial \mu)_\tau$ and explain why it should be related to the isothermal compressibility.

   b. (*Optional.*) The temperature τ and chemical potential μ fully determine the density $n(\tau, \mu)$, so that $(\partial n/\partial \mu)_\tau$ is independent of whether we hold V or N fixed. Justify this statement by a physical argument. More generally, how many parameters are required for a complete specification of the intensive properties (τ, μ, n, p) of the system?

   c. Derive a relationship between $(\partial n/\partial \mu)_\tau$ and κ_τ by the following steps:

      i. Show that
      $$\left(\frac{\partial n}{\partial \mu}\right)_\tau = -\frac{n}{V}\left(\frac{\partial V}{\partial \mu}\right)_{\tau,N}. \tag{1}$$

      ii. Derive the Maxwell relation
      $$\left(\frac{\partial V}{\partial \mu}\right)_{\tau,N} = -\left(\frac{\partial N}{\partial p}\right)_{\tau,V}. \tag{2}$$

      Hint: it is easier to calculate the inverse relation first, i.e. $(\partial \mu/\partial V)_{\tau,N} = -(\partial p/\partial N)_{\tau,V}$.

      iii. Use the definition of κ_τ to show that
      $$\left(\frac{\partial N}{\partial p}\right)_{\tau,V} = nV\kappa_\tau. \tag{3}$$

      iv. Combine your results to relate the density of states to the compressibility.

7. *Number fluctuations and compressibility.* The statistical fluctuations of a thermodynamic system in equilibrium are related to the system's response functions by a powerful theorem called the *fluctuation-dissipation theorem.* One example that you have seen is the relationship between fluctuations in energy and the heat capacity. Here, we will derive a similar relationship between number fluctuations and compressibility.

   a. Consider a generic system in thermal and diffusive equilibrium with a reservoir at temperature β^{-1} and chemical potential μ. Find an expression for the variance $(\Delta N)^2 \equiv \langle N^2\rangle - \langle N\rangle^2$ of the particle number N in terms of β, μ, and the Gibbs sum $\mathfrak{z}$. *Hint: find an expression for* $\langle N^2\rangle$ *in terms of derivatives of* $\mathfrak{z}$*, similar to our expression for* $\langle N\rangle$.

   b. Express ΔN in terms of the temperature τ, V, and $(d\langle n\rangle/d\mu)_{\tau,V}$, where $n = N/V$.

   c. What happens to the *fractional* fluctuations $(\Delta N)/N$ in the thermodynamic limit?

   d. Determine the relationship between the fractional number fluctuations and the isothermal compressibility κ_τ, using your result from problem 6. This is a manifestation of a more general relation known as the *fluctuation-dissipation theorem.*

   e. Simplify $(\Delta N)/N$ for the case of an ideal gas.

8. *Sound waves.* When a sound wave passes through a fluid (liquid or gas), the vibrations are fast compared to the time-scale for thermal equilibration via heat flow through the fluid. Hence, the local compressions of the fluid involved in the propagation of sound can be considered adiabatic.

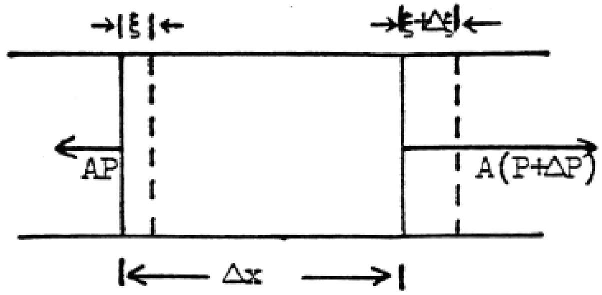

FIG. 1. A slab of fluid perturbed by the propagation of sound. A denotes the cross-sectional area of the slab.

a. By analyzing one-dimensional compressions and rarefactions of the system of fluid contained in a slab of thickness dx, show that the pressure $p(x,t)$ in the fluid depends on the position x and the time t so as to satisfy the wave equation

$$\frac{\partial^2 p}{\partial t^2} = u^2 \frac{\partial^2 p}{\partial x^2}, \tag{4}$$

where the velocity of sound propagation u depends on the equilibrium density ρ and the **adiabatic compressibility** $\kappa_\sigma \equiv -V^{-1}\left(\partial V/\partial p\right)_\sigma$.

b. Calculate the adiabatic compressibility κ_σ of an ideal gas in terms of its pressure p and its heat capacity ratio $\gamma = C_p/C_V$.

c. Find expressions for the velocity of sound u in an ideal gas…

   i. …in terms of γ, the mass m per molecule, and the temperature τ.

   ii. …in terms of γ and the rms velocity v_x^{rms} of the gas molecules in the direction of sound propagation.

d. Calculate the velocity of sound in nitrogen gas (N_2) at room temperature and pressure.

   i. Calculate the rms velocity v_x^{rms} in the direction of sound propagation.

   ii. The specific heat of N_2 at room temperature is well described by accounting for its translational and rotational degrees of freedom. (Vibrational excitation requires an energy much higher than $k_B \times 300$ K.) Based on this information, determine the value of γ.

   iii. Combine your results from i. and ii. to determine the sound velocity u.