

EXERCISE 4A: FUNDAMENTAL THERMODYNAMIC RELATION

Objectives:

- Derive the **fundamental thermodynamic relation** from laws of thermodynamics
- Understand what it means for a physical process to be **(ir)reversible**
- Work towards calculating the **equation of state** of the **ideal gas**

Reading: Kittel & Kroemer, Ch. 3

Last time:

- We defined the **Helmholtz Free Energy** $F = E - \tau\sigma$
- We showed that $F = -\tau \ln Z$

1. *Fundamental thermodynamic relation.*

The *First Law of Thermodynamics* is that energy is conserved. If one system is allowed to interact with another, energy can be exchanged in the form of either **work** W or **heat** Q . These two possible forms of energy exchange are summarized by the relation

$$dE = dW + dQ, \quad (1)$$

where W represents work done on the system and Q represents heat absorbed by the system.

- The symbol d emphasizes that neither W nor Q is a **state function**: the differences dW and dQ depend not only on the initial and final macrostates but also on the path taken between them. By contrast the energy E is a state function. List at least three other state functions that you have encountered so far in this course.
- The work $dW = -\mathbf{J} \cdot d\mathbf{x}$ arises from a displacement $d\mathbf{x}$ of an external parameter (i.e., a parameter of the Hamiltonian) resisted by a generalized force \mathbf{J} exerted by the system. By “generalized,” we mean that x need not have dimensions of length, and correspondingly J may not have dimensions of force, but the product Jx is always an energy.
 - Perhaps the most familiar example of an external parameter is the volume V of a gas. What is the corresponding generalized force? Justify your answer with the aid of a sketch. (There is space on the next page.)

- ii. If the external parameter we vary is a magnetic field $\mathbf{x} = \mathbf{B}$, what is the corresponding generalized force?
- c. In classical mechanics, work is the *only* way of changing a frictionless system's energy. The analog in statistical mechanics is an **adiabatic** process ($\dot{Q} = 0$).
- i. From a quantum mechanical perspective, an adiabatic process is one where the probability of occupying each eigenstate remains unchanged even while the associated energy eigenvalues may be changed by controlling external system parameters (e.g., magnetic field; volume). What macroscopic property (state function) then remains constant?

- ii. Qualitatively, for a given change in system parameters (e.g., doubling the volume of a gas), how should one effect the change to ensure that the process is adiabatic?
- iii. If the occupations of eigenstates change, the corresponding change in the system's energy is the **heat** dQ . Assume that the process leading to this change is **quasi-static**, i.e., slow enough that the system is always in a well-defined equilibrium macrostate. Use the definition of temperature to find an expression for dQ .
- d. Based on Eq. 1, write down the **fundamental thermodynamic relation** between dE , dV , and $d\sigma$ for a system at pressure p and temperature τ .

2. *Relations between state functions.* Next class, we will derive from first principles the **equation of state** of the ideal gas, i.e., the relationship between its pressure, volume, and temperature. First, let us derive some useful general relations between the state functions.

a. Following are some of the state functions that could be used to describe a homogeneous gas of N particles in thermal equilibrium:

- Volume V
- Pressure p
- Temperature τ
- Entropy σ
- Energy E
- Free energy F

If I gave you the values of all of these quantities, the system would be over-constrained. How many are necessary to specify the macrostate of the gas?

b. Based on the fundamental thermodynamic relation, the pressure is given by

$$p = - \left(\frac{\partial E}{\partial V} \right)_{\sigma} \quad (2)$$

However, we typically control the temperature and not the entropy. Derive an alternate expression for the pressure in terms of the Hemholtz free energy F and temperature τ .

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3. *Partition function of the ideal gas.* Consider a gas of N non-interacting particles in a cubic box of volume $V = L^3$. Recall that the energy eigenstates of a single particle in a three-dimensional box are given by

$$\varepsilon(n_x, n_y, n_z) = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2). \quad (3)$$

- a. Let z denote the partition function of a single particle in a one-dimensional box of length L (which we will calculate below). Find an expression for the partition function of N particles in a box of dimensions $L \times L \times L$ in terms of z . . .
- i. . . assuming that the particles are *distinguishable*

- ii. . . assuming that the particles are *indistinguishable*

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- b. Write out the partition function z for a single particle in a 1D box and simplify it by approximating the sum as an integral.