

Physics 127A – Homework Set 1

Due: 4pm, Wednesday, October 4

Thermodynamics/statmech review problems

Note: The problems in this set are review problems to help remind some basic thermodynamics and statistical mechanics. One can find this material presented in various ways in many textbooks, but I suggest to first try these problems on your own before consulting any texts.

Problem 1: Minimal experimental data to recover all thermodynamics (10 points)

In this problem, you will manipulate the main equation of thermodynamics encapsulating the first and second laws,

$$TdS = dU + pdV, \quad (1)$$

to obtain some thermodynamic identities and the minimal experimental data needed to recover all thermodynamics for a chunk of matter (can be gas or liquid or solid) described by parameters: particle number N , temperature T , volume V , and pressure p .

- a) Write dU in terms of dT and dV and then write dS in terms of dT and dV . From this, obtain expressions for $(\frac{\partial S}{\partial T})_V$ and $(\frac{\partial S}{\partial V})_T$ in terms of $(\frac{\partial U}{\partial T})_V$, $(\frac{\partial U}{\partial V})_T$, and the equation of state $p = p(T, V)$. By considering the mixed derivatives $\frac{\partial^2 S}{\partial T \partial V}$ and $\frac{\partial^2 S}{\partial V \partial T}$, prove the following identity:

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p. \quad (2)$$

We can thus write dU and dS in terms of the specific heat at constant volume $C_V \equiv (\frac{\partial U}{\partial T})_V$ and equation of state and integrate these equations to obtain $U(T_2, V_2) - U(T_1, V_1)$ and $S(T_2, V_2) - S(T_1, V_1)$. The integration can be done over any path from (T_1, V_1) to (T_2, V_2) , e.g., by first keeping volume constant at V_1 and varying temperature from T_1 to T_2 and then by keeping temperature constant at T_2 and varying volume from V_1 to V_2 . Write the corresponding integral expressions.

We conclude that all thermodynamics can be determined from measurements of the specific heat $C_V(T, V)$ and the equation of state $p(T, V)$.

- b) In fact, we do not need to know the whole $C_V(V, T)$. Indeed, by differentiating Eq. (2), derive the following relation between the volume derivative of the specific heat and the equation of state:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_V. \quad (3)$$

and then express $C_V(V, T) - C_V(V_0, T)$ as an integral from some reference volume V_0 to V . Thus, all thermodynamics is determined by specifying the equation of state $p(T, V)$ and the specific heat $C_V(V_0, T)$ at some reference volume V_0 .

- c) Using a) and b), calculate the specific heat and then the internal energy and entropy of the so-called van der Waals gas with equation of state

$$p = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2}. \quad (4)$$

by assuming that at large V (i.e., at very low density) its specific heat approaches the ideal gas specific heat $C_{V, \text{ideal gas}} = \frac{3}{2}Nk_B$. For the internal energy and entropy, calculate first $U(T_2, V_2) - U(T_1, V_1)$ and $S(T_2, V_2) - S(T_1, V_1)$; expressions for $U(T, V)$ and $S(T, V)$ can then be obtained by taking the reference $V_1 \rightarrow \infty$ where $U(T_1, V_1) \rightarrow U_{\text{ideal gas}}(T_1, V_1)$, $S(T_1, V_1) \rightarrow S_{\text{ideal gas}}(T_1, V_1)$, and one can use the ideal gas expressions for the internal energy and entropy (Sackur-Tetrode formula) reviewed in lecture 1.

- d) Use part c) to calculate the Helmholtz free energy of the van der Waals gas $F(T, V)$. Verify that $p = -\left(\frac{\partial F}{\partial V}\right)_T$.

Remark: In the van der Waals example, we assume throughout that the system is at a temperature above the so-called critical point, so we can use the van der Waals equation of state. Below the critical point, the equation of state needs to be modified to properly describe liquid-gas coexistence, which we will study in class.

Problem 2: Thermodynamics of a model classical paramagnet (10 points)

Consider a system consisting of N magnetic moments where each magnetic moment $i = 1, \dots, N$ is described by a three-component vector \mathbf{m}_i of fixed length $|\mathbf{m}_i| = \mu$. The energy in the magnetic field \mathbf{B} is given by

$$E = E[\{\mathbf{m}_i\}] = - \sum_{i=1}^N \mathbf{m}_i \cdot \mathbf{B}. \quad (5)$$

The partition sum is defined by integrating over all possible orientations of \mathbf{m} (i.e., all possible locations of \mathbf{m}/μ on the unit sphere). Calculate the free energy, average magnetization, and susceptibility of the system in the limit of a small field B .

Suggestion: It is convenient to use spherical coordinates with the z -axis oriented along the field, i.e., $\mathbf{m} = \mu(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$ and $\mathbf{B} = (0, 0, B)$. Note also that the statistical mechanics problem is defined here by the configuration integral over \mathbf{m} only; i.e., there is no "kinetic energy" in this problem (more microscopically, including such kinetic energy and integrating over the corresponding momenta would give only a factor that is independent of B and hence is not important for discussing magnetic properties).