

Problem 1. (40 points)

The macrostates of a system can be specified by the total energy U , the volume V , and the number of particles N .

3 pts A. Write down the fundamental thermodynamic relation for such a system.

$$dU = TdS - PdV + \mu dN$$

In the microcanonical ensemble, the thermodynamic variables are derived from the number of accessible microstates $\Omega(U, V, N)$ with energy U , volume V , and number N .

6 pts B. Explain how to get each of the following thermodynamic variables directly from Ω .

entropy $S = \log \Omega$

temperature T : $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V, N}$

pressure P $P = T \left(\frac{\partial S}{\partial V}\right)_{U, N}$

chemical potential μ $\mu = T \left(\frac{\partial S}{\partial N}\right)_{U, V}$

The probability P_i of a microstate i with energy E_i and number N_i in the microcanonical ensemble is

$$P_i = \begin{cases} 1/\Omega(U, N) & \text{if } E_i = U \text{ and } N_i = N \\ 0 & \text{otherwise.} \end{cases}$$

4 pts C. Calculate the information entropy $S_{\text{info}} = -\sum_i P_i \log P_i$ for this probability distribution.

$$\begin{aligned} S_{\text{info}} &= -\sum_i \delta_{E_i, U} \delta_{N_i, N} \frac{1}{\Omega} \log \frac{1}{\Omega} \\ &= -\frac{1}{\Omega} (-\log \Omega) \sum_i \delta_{E_i, U} \delta_{N_i, N} \\ &= \frac{1}{\Omega} \log \Omega \Omega = \log \Omega \end{aligned}$$

In the canonical ensemble, the thermodynamic variables are derived from the partition function $Z(T, V, N)$ for N particles in volume V at temperature $T = 1/\beta$.

3 pts D. Write down the thermodynamic relation for the Helmholtz free energy $F = U - TS$.

$$dF = (TdS - PdV + \mu dN) - (TdS + SdT)$$

$$= -SdT - PdV + \mu dN$$

3 pts E. Explain how to get each of the following thermodynamic variables directly from Z .

Helmholtz free energy $F = -\frac{1}{\beta} \log Z$

entropy $S = -\left(\frac{\partial F}{\partial T}\right)_{V, N}$

The probability P_i of a microstate i with energy E_i and number N in the canonical ensemble is

$$P_i = \frac{1}{Z} \exp(-\beta E_i), \quad \text{where } Z = \sum_i \exp(-\beta E_i).$$

6 pts F. Express the energy U of the system as a sum over microstates. Use it to derive an expression for U in terms of a partial derivative of Z .

$$U = \sum_i P_i E_i = \frac{1}{Z} \sum_i E_i e^{-\beta E_i}$$

$$= \frac{1}{Z} \left(-\frac{\partial}{\partial \beta}\right) \sum_i e^{-\beta E_i} = -\frac{1}{Z} \left(\frac{\partial}{\partial \beta} Z\right)_{V, N}$$

6 pts G. Calculate the information entropy S_{info} for the probability distribution of the canonical ensemble. Express it in terms of the extensive thermodynamic variables F and U .

$$S_{\text{info}} = -\sum_i P_i \log P_i = -\sum_i \frac{1}{Z} e^{-\beta E_i} (-\log Z - \beta E_i)$$

$$= \frac{1}{Z} \log Z \sum_i e^{-\beta E_i} + \frac{\beta}{Z} \sum_i E_i e^{-\beta E_i}$$

$$= \frac{1}{Z} \log Z \cdot Z + \beta U = -\beta F + \beta U$$

$$= -\beta(F - U)$$

In the grand canonical ensemble, the thermodynamic variables are derived from the grand partition function $\mathcal{Z}(T, V, \mu)$ with temperature $T = 1/\beta$, volume V , and chemical potential μ . The grand potential $\Phi = U - TS - \mu N$ satisfies $\mathcal{Z} = \exp(-\beta\Phi)$.

3 pts H. Write down the thermodynamic relation for the grand potential Φ .

$$d\Phi = (\cancel{TdS} - PdV + \cancel{\mu dN}) - (\cancel{TdS} + SdT) - (\cancel{\mu dN} + Nd\mu)$$

$$= -SdT - PdV - Nd\mu$$

3 pts I. Explain how to get each of the following thermodynamic variables directly from Φ .

entropy S $S = - \left(\frac{\partial \Phi}{\partial T} \right)_{V, \mu}$

pressure P $P = - \left(\frac{\partial \Phi}{\partial V} \right)_{T, \mu}$

number of particles N $N = - \left(\frac{\partial \Phi}{\partial \mu} \right)_{T, V}$

3 pts J. What is the probability P_i of a microstate i with energy E_i and number N_i in the grand canonical ensemble with temperature $T = 1/\beta$, volume V , and chemical potential μ ?

$$P_i = \frac{1}{\mathcal{Z}} e^{-\beta E_i + \beta \mu N_i}$$

where $\mathcal{Z} = \sum_i e^{-\beta E_i + \beta \mu N_i}$

Problem 2. (30 points)

A quantum spin system consists of N spins with spin $\frac{1}{2}$ and magnetic momentum μ in a magnetic field B along the z -axis. The Hamiltonian is

$$H = - \sum_{n=1}^N (\mu_z)_n B.$$

Each of the magnetic moment operators $(\mu_z)_n$ has two eigenvalues: $+\mu$ and $-\mu$. The microstates i can be specified by a list of the N signs of the eigenvalues, such as $(+ - + + - \dots - + -)$.

3 pts A. Identify the microstate i with the minimum total energy E_i , and give its energy.

$$i = (++++ \dots ++); \quad E_i = -N\mu B$$

3 pts B. Identify the microstate i with the maximum total energy E_i , and give its energy.

$$i = (-----); \quad E_i = -N(-\mu)B = +N\mu B$$

3 pts C. How many microstates are there with total energy $E_i = 0$? (Simplify the expression using the approximation $n! \approx (n/e)^n$.)

$$\frac{N}{2} \text{ spins } +, \frac{N}{2} \text{ spins } - \quad \binom{N}{N/2} = \frac{N!}{[(N/2)!]^2} \approx \frac{(N/e)^N}{[(N/2e)^{N/2}]^2} = 2^N$$

3 pts D. What is the entropy $S(U)$ at the minimum energy, the maximum energy, and $U = 0$?

$$U = -N\mu B: 1 \text{ state} \Rightarrow S = \log 1 = 0$$

$$U = +N\mu B: 1 \text{ state} \Rightarrow S = \log 1 = 0$$

$$U = 0 : 2^N \text{ states} \Rightarrow S = -\log(2^N) = N \log 2$$

3 pts E. Write down the partition function for a single spin in thermal equilibrium at temperature $T = 1/\beta$.

$$Z_1 = \sum_{\pm} e^{-\beta(\pm\mu)B} = e^{+\beta\mu B} + e^{-\beta\mu B} = 2 \cosh(\beta\mu B)$$

3 pts F. Write down the partition function for the N spins in thermal equilibrium at temperature $T = 1/\beta$.

$$Z_N = Z_1^N = [2 \cosh(\beta\mu B)]^N$$

The entropy, energy, and magnetization of the spin system in the thermodynamic limit are

$$S = N \left[\log(2 \cosh(\beta\mu B)) - \beta\mu B \tanh(\beta\mu B) \right]$$

$$U = -N\mu B \tanh(\beta\mu B).$$

$$M = N\mu \tanh(\beta\mu B).$$

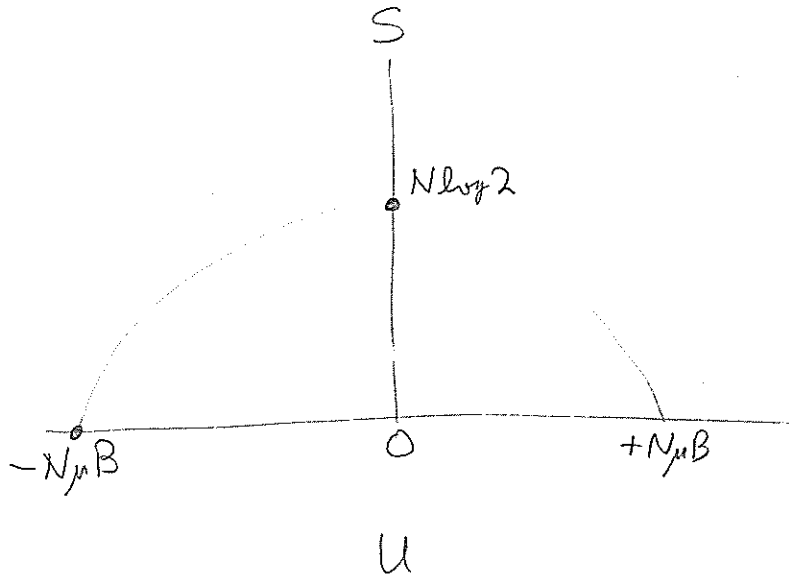
(The fundamental thermodynamic relation is $dU = T dS - M dB$, but you won't need it.)

By eliminating β , S could in principle be expressed as a function of U .

5 pts

F. Make a sketch of the entropy S as a function of U .

Label the maximum and minimum values on both axes.



2 pts G. Identify the regions of U in which the temperature T is positive and the regions of U in which the temperature T is negative.

$$-N\mu B < U < 0 : \frac{\partial S}{\partial U} > 0 \implies T \text{ positive}$$

$$0 < U < +N\mu B : \frac{\partial S}{\partial U} < 0 \implies T \text{ negative}$$

Suppose this spin system, which consists of N spins at temperature T , is brought into thermal contact with a second similar spin system that consists of N' spins at temperature T' . The two systems will eventually come to thermal equilibrium at a common temperature T_{eq} .

5 pts H. Write down the equation that determines T_{eq} .
(Simplify it by expressing it in terms of N'/N , $\mu B/kT$, $\mu B/kT'$, and $\mu B/kT_{eq}$ only.)

$$\begin{aligned} U_{total} &= -N\mu B \tanh(\mu B/kT) - N'\mu B \tanh(\mu B/kT') \\ &= -N\mu B \tanh(\mu B/kT_{eq}) - N'\mu B \tanh(\mu B/kT_{eq}) \end{aligned}$$

$$\tanh(\mu B/kT) + \frac{N'}{N} \tanh(\mu B/kT') = \left(1 + \frac{N'}{N}\right) \tanh(\mu B/kT_{eq})$$

Problem 3. (30 points)

Suppose the only term in the Hamiltonian H that depends on a generalized coordinate q with range $-\infty < q < +\infty$ is Aq^2 .

- 5 pts A. Use the canonical ensemble to derive the contribution $\langle Aq^2 \rangle$ of that term to the energy U . The following Gaussian integrals may be useful:

$$\int_{-\infty}^{+\infty} dx \exp(-ax^2) = \sqrt{\frac{\pi}{a}}, \quad \int_{-\infty}^{+\infty} dx x^2 \exp(-ax^2) = \frac{1}{2} \sqrt{\frac{\pi}{a^3}}, \quad \int_{-\infty}^{+\infty} dx x^4 \exp(-ax^2) = \frac{3}{4} \sqrt{\frac{\pi}{a^5}}.$$

$$\begin{aligned} \langle Aq^2 \rangle &= \frac{\int dw Aq^2 e^{-\beta H}}{\int dw e^{-\beta H}} = \frac{\int_{-\infty}^{\infty} dq Aq^2 e^{-\beta Aq^2}}{\int_{-\infty}^{\infty} dq e^{-\beta Aq^2}} \\ &= \frac{A \cdot \frac{1}{2} \sqrt{\pi / (\beta A)^3}}{\sqrt{\pi / \beta A}} = \frac{1}{2\beta} = \frac{1}{2} kT \end{aligned}$$

A simple classical model for a gas consisting of N identical atoms in a volume V is point particles with a potential $V_{\text{ext}}(\vec{r})$ that confines them to that region. The potential is 0 inside the region of volume V and $+\infty$ outside. The Hamiltonian for the atoms is

$$H = \sum_{n=1}^N \left(\frac{1}{2m} \vec{p}_n^2 + V_{\text{ext}}(\vec{r}_n) \right).$$

- 5 pts B. Use the equipartition theorem to deduce the energy U of the gas.

3N terms quadratic in momenta, $V_{\text{ext}} = 0$ in accessible region

$$U = 3N \cdot \frac{1}{2} kT + 0 = \frac{3}{2} NkT$$

A simple classical model for a solid consisting of N identical atoms is point particles bound with binding energy ε to the sites of a cubic lattice with spacing a and attracted to the lattice sites by a harmonic potential with angular frequency ω . The Hamiltonian for the atoms is

$$H = \sum_{n=1}^N \left(\frac{1}{2m} \vec{p}_n^2 + \frac{1}{2} m\omega^2 (\vec{r}_n - \vec{r}_{n,\text{eq}})^2 - \varepsilon \right),$$

where $\vec{r}_{n,\text{eq}}$ is the equilibrium position of the n 'th atom, which is on one of the lattice sites.

- 5 pts C. Use the equipartition theorem to deduce the energy U of the solid.

3N terms quadratic in momenta

3N terms quadratic in shifted coordinates

$$U = 3N \cdot \frac{1}{2} kT + 3N \cdot \frac{1}{2} kT + N(-\varepsilon) = N(3kT - \varepsilon)$$

There is a phase transition between the solid and the gas.

If the system is a homogeneous gas, its pressure, entropy, and chemical potential are

$$\begin{aligned} P &= NkT/V, \\ S &= Nk \left[\log \left((V/N) (mkT/2\pi\hbar^2)^{3/2} \right) + 5/2 \right], \\ \mu &= -kT \log \left((V/N) (mkT/2\pi\hbar^2)^{3/2} \right). \end{aligned}$$

(They satisfy $TS + N\mu = \frac{5}{2}NkT$.)

If the system is a homogeneous solid, its volume is fixed at $V = Na^3$. Its pressure adjusts automatically to balance the pressure of whatever it is contact with. A thermodynamically consistent model for its entropy and chemical potential is

$$\begin{aligned} S &= 3Nk \log(kT/\hbar\omega), \\ \mu &= -3kT \left[\log(kT/\hbar\omega) - 1 \right] - \epsilon. \end{aligned}$$

(They satisfy $TS + N\mu = 3NkT - N\epsilon$.)

5 pts E. Use the equilibrium condition on the fugacities $\exp(\mu/kT)$ of the coexisting solid and gas to determine the pressure $P_{\text{coex}}(T)$ of the gas at the phase transition as a function of the temperature T .

$$\exp(\mu_{\text{gas}}/kT) = \exp(\mu_{\text{solid}}/kT)$$

$$\frac{N}{V} \left(\frac{2\pi\hbar^2}{mkT} \right)^{3/2} = \left(\frac{\hbar\omega}{kT} \right)^3 e^{3 - \epsilon/kT}$$

$$\frac{N}{V} = \frac{P}{kT} \implies P_{\text{coex}}(T) = kT \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \left(\frac{\hbar\omega}{kT} \right)^3 e^{3 - \epsilon/kT}$$

The Clausius-Clapeyron equation for the slope of the coexistence pressure is

$$\frac{d}{dT} P_{\text{coex}}(T) = \frac{L(T)}{T [V_{\text{gas}}(T, P_{\text{coex}}(T)) - V_{\text{solid}}]}$$

where $L(T)$ is the latent heat required to change the system from 100% solid to 100% gas.

5 pts F. Express $L(T)$ in terms of more basic thermodynamical variables for the solid and the gas.

(The expression can be simplified using the identities in parentheses above.)

$$\begin{aligned} L(T) &= T [S_{\text{gas}} - S_{\text{solid}}] = T \left[\left(-N \mu_{\text{gas}} + \frac{5}{2} NkT \right) - \left(-N \mu_{\text{solid}} + 3NkT - \epsilon \right) \right] \\ &= -\frac{1}{2} NkT + N\epsilon = N \left(\epsilon - \frac{1}{2} kT \right) \end{aligned}$$

5 pts G. Suppose T is large enough that $V_{\text{gas}} \gg V_{\text{solid}}$. Use this to separate the variables P and T in the Clausius-Clapeyron equation. Express the solution for $P_{\text{coex}}(T)$ in terms of the exponential of a definite integral over temperature.

$$\frac{d}{dT} P = \frac{L'}{TV_{\text{gas}}} = \frac{L}{T(NkT/P)} \implies \frac{dP}{P} = \frac{L(T)}{NkT^2} dT$$

$$\int_{T_0}^T \frac{d P_{\text{coex}}(T')}{P_{\text{coex}}(T')} = \log \frac{P_{\text{coex}}(T)}{P_{\text{coex}}(T_0)} = \int_{T_0}^T \frac{L(T')}{NkT'^2} dT' \quad P_{\text{coex}}(T) = P_{\text{coex}}(T_0) \exp \left(\int_{T_0}^T \frac{L(T')}{NkT'^2} dT' \right)$$