

Statistical Physics: Tutorial 1

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A: Core problems

1. Internal energy and expansion The first law of thermodynamics can be written as

$$dE = C_V \, dT + \left. \frac{\partial E}{\partial V} \right|_T dV$$

as well as the standard form dE = T dS - P dV. Use the standard form to obtain

$$\left.\frac{\partial E}{\partial V}\right|_T = T \left.\frac{\partial S}{\partial V}\right|_T - P;$$

then rewrite the partial derivative on the RHS using a Maxwell relation derived via the free energy, dF = -S dT - P dV, to prove that

$$dE = C_V \, dT + \left(T \left. \frac{\partial P}{\partial T} \right|_V - P \right) \, dV.$$

Hence show that an imperfect gas with the equation of state P(V-b) = NkT, where b is a constant, has an internal energy that depends only on temperature, provided C_V also depends only on T. If this gas undergoes Joule expansion (slow expansion into a vacuum), how does the temperature change? If it undergoes adiabatic compression, how does the temperature depend on the volume if C_V is a constant? [compute this using the path independence of thermodynamic variables: consider e.g. isothermal compression, then heating at constant V]

2. The Gibbs Entropy Consider the function

$$S(\{p_i\}) = -k \sum_{i=1}^{r} p_i \ln p_i,$$

where p_i are the probabilities of the r distinct possible outcomes of some procedure.

- (a) Sketch the form of S as a function of p_1 for r = 2.
- (b) Show that S has its maximum value when the p_i are all equal to 1/r [hint: use Lagrange multipliers. What constraint must the p_i satisfy?].
- (c) Show that the value of S is increased when any two of the probabilities are changed in such a way as to reduce their difference.
- 3. Ensemble relation of Gibbs to Boltzmann entropies In a system the Boltzmann entropy of any macrostate is given by

$$S = k \ln \Omega$$

where Ω is the weight of the macrostate (number of associated microstates).

Now consider an *ensemble*, consisting of m such systems, each with q possible microstates available. The number of systems in each possible microstate i, m_i , defines the frequentist probability for that microstate, $p_i = m_i/m$. Derive an expression for the Boltzmann entropy of the entire ensemble, specified by $\{m_i\}$. You will need the number of ways of assigning states to the *m* systems, using a multinomial coefficient

$$\Omega = \frac{m!}{m_1! \, m_2! \dots m_q!} \; .$$

Use Stirling's approximation to show that the Boltzmann entropy of the ensemble per system takes the Gibbs form when m is large:

$$S(\{p_i\}) = -k \sum_{i=1}^{r} p_i \ln p_i$$

4. Maximum entropy probabilities In a certain game a player can score any integer n = 0, 1, ...and it is known that the mean score is μ . Use the method of Lagrange multipliers to show that, knowing the mean, the maximum-entropy probability distribution for the score is

$$p_n = A \exp(-\lambda n)$$

where A, λ are constants. By imposing the relevant constraints determine these constants and show that

$$p_n = \frac{\mu^n}{(1+\mu)^{n+1}}$$
.

B: Further problems

1. Stirling's formula and entropy

(a) Starting from Stirling's formula

$$\ln(N!) \simeq N[\ln N - 1]$$

show using Boltzmann's formula for entropy that, for a lattice of N independent (weakly interacting) spins, each either up or down, the entropy is given by

$$S = -kN[c\ln c + (1-c)\ln(1-c)]$$

where c is the fraction of up spins

Rederive this result from the Gibbs entropy, first proving the fact that for a weakly interacting system the Gibbs entropy reduces to $N S_G(1)$, where $S_G(1)$ is the Gibbs entropy of a single spin.

(b) From Stirling's formula, show that if, instead of having spins, each lattice site can be either empty, or occupied by a particle of type 1 (concentration c_1) or occupied by a particle of type 2 (concentration c_2), then

$$S = -kN[c_1 \ln c_1 + c_2 \ln c_2 + (1 - c_1 - c_2) \ln(1 - c_1 - c_2)]$$

Rederive this result using the Gibbs entropy.

2. Thermodynamic representation of the chemical potential We have defined the chemical potential as

$$\mu = \left(\frac{\partial \overline{E}}{\partial \overline{N}}\right)_{S,V}$$

show that equivalent representations are

$$\mu = -T\left(\frac{\partial S}{\partial \overline{N}}\right)_{\overline{E},V} = \left(\frac{\partial F}{\partial \overline{N}}\right)_{V,T} = \left(\frac{\partial G}{\partial \overline{N}}\right)_{P,T}$$

Hence establish that $G(T, P, \overline{N}) = \overline{N}\mu$. For this part (tricky) you will have to invoke extensivity of the Gibbs free energy.

- 3. The chemical potential in equilibrium Consider two systems juxtaposed so that particles may be freely exchanged between them. By maximising the Gibbs entropy, show that both systems have equilibrium grand canonical distributions characterised by the same value of μ . Hint: you should consider the composite system of the two systems.
- 4. Canonical distribution for a system with free boundaries Consider a fluid in a container whose walls are flexible so that its volume may take on any of a set of values $\{V_{\alpha}\}$. Suppose that the temperature and pressure of the environment are such that the mean energy and mean volume of the system are \overline{E} , \overline{V} respectively. Establish the probability p_i of finding the fluid to be in a microstate with a particular volume and energy. Identify the two Lagrange multipliers appearing in your results. Show that the set of probabilities thus assigned are such as to minimise the Gibbs free energy of the system for the given temperature and pressure.