

Problem Set 4 - Blackbody radiation

(Dated: PHYS403, Spring 2024)

I. Variational derivation of micro-state probabilities

In this problem, you will explore an alternate way to derive the thermal distribution over microstates in the Grand-Canonical ensemble, as a variational problem.

Consider a system with microstates labeled by index n , and denote the energy and particle number for micro-state n as E_n , and N_n respectively.

Using the method of Lagrange multipliers ¹, find the probability distribution on microstates, p_n that has maximal Shannon entropy, $S[p_n] = -\sum_n p_n \log p_n$ subject to the constraints that:

- (A) the probabilities are normalized: $\sum_n p_n - 1 = 0$
- (B) the average energy is \bar{E} : $\sum_n p_n E_n - \bar{E} = 0$
- (C) the average particle number is \bar{N} : $\sum_n p_n N_n - \bar{N} = 0$

Namely, introduce Lagrange multipliers α, β, γ to enforce each of the above constraints, and maximize the objective function:

$$S[p_n] - \alpha(\sum_n p_n - 1) - \beta(\sum_n p_n E_n - \bar{E}) - \gamma(\sum_n p_n N_n - \bar{N})$$

with respect to the p_n 's (note you may simply leave the Lagrange multipliers α, β, γ as unknown variables, you don't need to solve for their extremal values). Show that the form matches that of the Grand Canonical ensemble, and interpret the Lagrange multipliers α, β, γ in terms of thermodynamic and/or statistical-mechanics quantities.

Food for thought (not graded): can you think of an argument for why this variational approach should match the stat-mech derivation I gave in class?

II. Surface tension of a balloon

Surface tension: thermodynamic properties of the interface between two phases are described by a state function called the surface tension σ . It is defined in terms of the work required to increase the surface area by an amount dA through $dW = \sigma dA$. By considering the work done against surface tension in an infinitesimal change in radius, show that the pressure inside a balloon of radius R is larger than outside pressure by $2\sigma/R$.

¹ Recall that maximizing a function $f(x)$ subject to the constraint $C(x) = 0$ can be solved by introducing a Lagrange multiplier λ and extremizing $g(x, \lambda) = f(x) - \lambda C(x)$ with respect to both x and λ . To see the idea behind this, note that the extremal condition for λ is $0 = \partial g / \partial \lambda = C(x)$ enforces the constraint $C(x) = 0$.

III. Surfactants

Surfactant molecules are the main active ingredients in soaps and detergents, and function to reduce the surface tension between oil and water (which would otherwise not mix due to their large surface tension, σ). Consider a 2d interface of area A between oil and a volume V of water with a (3d) density n of surfactant molecules dissolved in it. Suppose a surfactant lowers its energy an amount ε_0 when it moves from the water solution to the oil/water interface. *Terminology: a surfactant molecule that is “stuck” to the interface is referred to as being “adsorbed”.* The goal of this problem will be to compute the reduction in surface tension of the oil/water interface as a function of temperature, T using the following steps:

1. First, compute the grand partition function, $\mathcal{Z}_{G.C.}^{(d)}(\mu, T)$, of an ideal gas of particles moving in d dimensional box with volume V_c and a uniform potential ε_d , at chemical potential μ and temperature T . Simplify your answer in terms of the thermal DeBroglie wavelength λ of the surfactant molecule.
Below we will be interested in using this result in 3d for the surfactants in solution with $V_3 = V$ and $\varepsilon_3 = 0$, and in 2d with $V_2 = A$ and $\varepsilon_2 = -\varepsilon_0$ for the surfactants adsorbed at the interface.
2. Assume we can treat the surfactant molecules in solution as a 3d ideal gas. Treating this problem in the grand-canonical ensemble. Compute the 3d density $n = \langle N \rangle / V$ of the surfactant molecules in the water solution as a function of their chemical potential μ and temperature T . *Hint: recall how to compute the expected number of particles by taking derivatives of the partition function*
3. Assume we can also treat the surfactant molecules that are adsorbed onto the oil/water interface as an ideal gas, but which can only move in two dimensions (within the interface), and have a lower energy $-\varepsilon_0$ relative to the particles in solution. From this, find the surface area density, n_s , of surfactant molecules at chemical potential μ and temperature T (don't forget to account for the fact that an adsorbed molecule has lower energy than one dissolved in solution). *Note that the adsorbed molecules reduce the surface tension of the oil/water interface by an amount: $\Delta\sigma = -\varepsilon_0 n_s$, since each adsorbed molecule lowers the energy of the interface.*
4. How do expect the surfactant's ability to mix oil and water will change as we heat up the solution?