Canonical Ensembles

1. *Non-harmonic Gas:* Consider a gas of N non-interacting atoms in a d-dimensional box of "volume" V, with a kinetic energy

$$\mathcal{H}=\sum_{i=1}^{N} A\left|\vec{p}_i\right|^s ,$$

where $\vec{p}_i$ is the momentum of the i^{th} particle.

(a) Calculate the classical partition function $Z(N,T)$ at a temperature T. (*You don't have to keep track of numerical constants in the integration.*)

(b) Calculate the pressure and the internal energy of this gas. (Note how the usual equipartition theorem is modified for non-quadratic degrees of freedom.)

(c) Now consider N diatomic molecules, each with energy

$$\mathcal{H}_i=A\left(\left|\vec{p}_i^{\,(1)}\right|^s+\left|\vec{p}_i^{\,(2)}\right|^s\right)+K\left|\vec{q}_i^{\,(1)}-\vec{q}_i^{\,(2)}\right|^t ,$$

where the superscripts refer to the two particles in the molecule. (Note that this unrealistic potential allows the two atoms to occupy the same point.) Calculate the expectation value $\left\langle\left|\vec{q}_i^{\,(1)}-\vec{q}_i^{\,(2)}\right|^t\right\rangle$, at temperature T.

(d) For the gas in (c) calculate the heat capacity ratio ratio $\gamma=C_P/C_V$.

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2. *Curie Susceptibility:* Consider N non-interacting quantized spins in a magnetic field $\vec{B}=B\hat{z}$, and at a temperature T. The work done by the field is given by $-BM_z$, with a magnetization $M_z=\mu\sum_{i=1}^{N} m_i$. For each spin, m_i takes only the $2s+1$ values $-s,-s+1,\cdots,s-1,s$.

(a) Calculate the Gibbs partition function $\mathcal{Z}(T,B)$. (Note that the ensemble corresponding to the macro-state (T,B) includes magnetic work.)

(b) Calculate the Gibbs free energy $G(T,B)$, and show that for small B,

$$G(B)=G(0)-\frac{N\mu^2 s(s+1)B^2}{6k_BT}+\mathcal{O}(B^4).$$

(c) Calculate the zero field susceptibility $\chi = \partial M_z/\partial B|_{B=0}$, and show that is satisfies *Curie's law*

$$\chi = c/T.$$

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3. *Surfactant Adsorption:* A dilute solution of surfactants can be regarded as an ideal three dimensional gas. As surfactant molecules can reduce their energy by contact with air, a fraction of them migrate to the surface where they can be treated as a two dimensional ideal gas. Surfactants are similarly adsorbed by other porous media such as polymers and gels with an affinity for them.

(a) Consider an ideal gas of classical particles of mass m in d dimensions, moving in a *uniform* attractive potential of strength ε_d. By calculating the partition function, or otherwise, show that the chemical potential at a temperature T and particle density n_d, is given by

$$\mu_d = -\varepsilon_d + k_B T \ln\left[n_d \lambda(T)^d\right], \quad \text{where} \quad \lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}}.$$

(Note that the integrals appearing in the partition function can be made dimensionless by using $\int dqdp/h$. *Classical* statistical mechanics does not specify h which could itself depend on d. Within *quantum* statistical mechanics, h is uniquely identified with Planck's constant.)

(b) If a surfactant lowers its energy by ε_0 in moving from the solution to the surface, calculate the concentration of floating surfactants as a function of the solution concentration $n\,(= n_3)$, at a temperature T.

(c) Gels are formed by cross-linking linear polymers. It has been suggested that the porous gel should be regarded as *fractal*, and the surfactants adsorbed on its surface treated as a gas in d_f dimensional space, with a non-integer d_f. Can this assertion be tested by comparing the relative adsorption of surfactants to a gel, and to the individual polymers (presumably one dimensional) before cross-linking, as a function of temperature?

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Suggested Reading: Huang, Chapter 7.