Thermodynamics HW #10
Due Friday, November 8th

1. The partition function Z is introduced simply as a normalization factor relating "Boltzmann factors" $e^{-\frac{E}{kT}}$ to probabilities. It turns out, however, that the partition function is a key quantity in statistical physics. Many quantities of thermodynamic interest are related to the partition function by surprisingly simple formulas. Show, for example, that the average energy $\langle U \rangle$ of a thermodynamic system in contact with a reservoir with a temperature T is given by the formula

$$\langle U \rangle = -(d/d\beta) \ln Z$$

where Z is the partition function and $\beta \equiv \frac{1}{kT}$.

2. If we let our system contain a large number of particles, we know that under normal conditions the system never strays far from its expectation values, so that we can say $U = \langle U \rangle$. Though the energy U is a fundamental thermodynamic quantity, it is less accessible experimentally than, say, the heat capacity C_v, which can be measured by simply adding heat to system and noting the resulting temperature change. Show further that C_v can be calculated from the partition function via

$$C_v = k\sigma^2 (d^2/d\sigma^2) \ln Z$$

where k is Boltzmann's constant and σ is any constant multiple of β.

3. Though the partition function of a microscopic system (like a single harmonic oscillator) can be easy to calculate, the partition function of a macroscopic system can be quite difficult because of the large number of degrees of freedom it contains. Oftentimes, however, the system can be broken up into smaller subsystems that do not interact with other and as a result the partition function takes on a simplified form.

In detail, let us suppose a microstate of our system is described by a series of indices $n_1, n_2, \ldots, n_i, \ldots, n_M$ so that we can specify a microstate by specifying a value for each of the n_i[1,2]. Further suppose that the energy $E(n_1, n_2, \ldots, n_M)$ of a microstate is a *sum* of terms that only depend on one index, i.e.

$$E(n_1, n_2, \ldots, n_M) = E_1(n_1) + E_2(n_2) + \cdots + E_N(n_M)$$

[3]. It is in this sense that we say that the i^{th} subsystem "does not interact" with the j^{th} subsystem, where $j \neq i$.

Assuming that all possible combinations of indices are allowed[4], show then that the partition function Z of this system *factorizes* so that

$$Z = Z_1 \times Z_2 \times \cdots \times Z_M$$

[1] e.g. if $M = 3$ we could specify a microstate by specifying, e.g., $n_1 = 22, n_2 = 41, n_3 = 88$

[2] For concreteness suppose that the i^{th} index runs from $1, 2, \ldots, M_i$.

[3] For example, the energy of a collection of gas particles can to a good approximation be written as a sum of the kinetic energies plus vibrational energy plus rotational energy. In this case $M = 3$ and E_1 might be the kinetic energy of *all* the particles, and likewise for the other two.

[4] This ignores any difficulties associated with the possible *indistinguishability* of the particles in the system. If we consider a gas, which is by definition low density, we can in a rough sense ignore the possibility of multiple occupation of a single state, and thus correct for indistinguishability by inserting the $1/N!$ "Gibbs Factor" into the partition function at the end.

where Z_i depends only on E_i. Show that this implies that the energy U (and thus the heat capacity C_v) of the system can be partitioned into a *sum* $U_1 + U_2 + \cdots + U_M$ (and $C_{v1} + C_{v2} + \cdots + C_{vM}$) different pieces, each depending only on one particular E_i.

4. Many systems also can (at least approximately) represented as a collection of non-interacting particles. In this case, we would like to treat each index n_i as a *vector* of indices $\mathbf{n}_i = [\mathbf{n}_i]_1, [\mathbf{n}_i]_2, \ldots, [\mathbf{n}_i]_N$ of length N, the number of particles in the system. The j^{th} component $[\mathbf{n}_i]_j$ of the vector specifies a quantum number for the j^{th} particle. So long as the particles do not interact, the energy E_i for a system in a microstate $\mathbf{n}_1, \mathbf{n}_2, \ldots, \mathbf{n}_i, \ldots, \mathbf{n}_M$ is given by

$$E_i(\mathbf{n}_i) = \sum_{j=1}^{N} \varepsilon_i([\mathbf{n}_i]_j)$$

Show then that the partition function Z_i simplifies to

$$Z_i = z_i^N$$

where z_i is indepedent of N and is the partition function for the i^{th} index of a single particle. Show that this in turn implies that i^{th} *molar* heat capacity $(c_v)_i$ is given by

$$(c_v)_i = R\sigma^2 (d^2/d\sigma^2) \ln z_i \tag{1}$$

where $R \equiv N_A k$ is the universal gas constant.