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A gas is composed of an atomic species A. At low temperature the atoms mostly bind in pairs to form diatomic molecules A_2, but at higher temperatures the molecules can thermally dissociate into individual atoms *via* the reversible process

$$A_2 \rightleftharpoons A + A.$$

The binding energy of the diatomic molecule is E_0. The mass of an isolated A atom is m and that of a diatomic molecule is $2m$. We wish to compute the fraction of molecules that are thermally dissociated when N atoms of A are held in thermal equilibrium at temperature T in a container of volume V.

In working this problem you may assume that the temperature is high enough that we can use classical Boltzmann statistics, and that N and V are large enough that we are in the thermodynamic limit. You may also neglect any rotational or vibrational modes of the diatomic molecule.

a) Write down the expression giving the partition function $Z_{N,\mathrm{atoms}}$ of a gas of N identical atoms of mass m at temperature T in a container of volume V. Evaluate the integral it contains, and so express $Z_{N,\mathrm{atoms}}$ as a product of powers of kT, m, the reduced Planck constant $\hbar$, V and $N!$. Here k is Boltzmann's constant.

b) Write down the partition function Z_N for the partially dissociated gas of N atoms as a sum over terms, each corresponding to there being N_1 single atoms and N_2 diatomic molecules (with $N_1 + 2N_2 = N$).

c) To deal with the constraint $N_1 + 2N_2 = N$, introduce a chemical potential μ and form the grand-canonical partition function

$$\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} Z_N e^{\mu N/kT}.$$

Evaluate $\mathcal{Z}(\mu, V, T)$ in closed form.

d) From your result in part (c) compute N_1 and N_2 in terms of μ, and hence show that

$$\frac{(N_1)^2}{N_2} = K e^{-E_0/kT}.$$

where K is a number, depending on m, kT, V and $\hbar$ that you should evaluate explicitly.