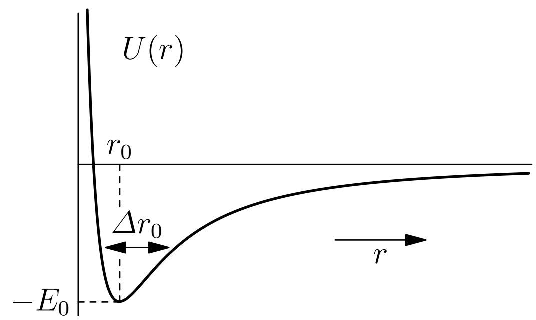
J03T.2—Krypton Molecule Formation

Problem

Krypton atoms are rather heavy and reasonably polarizable. The potential between two krypton atoms is shown in the figure



In the limit in which the mass of the Kr atom is very large, there will at low energies and temperatures be an equilibrium of the form

$$\mathrm{Kr} + \mathrm{Kr} \leftrightarrow \mathrm{Kr}_2$$

a) The classical partition function of two krypton atoms inside a volume V can be written as

$$Z_2 = \left(1 + \frac{K}{V}\right) Z_2^{\mathrm{id}}$$

where Z_2^{id} is the partition sum of two free atoms. How is the constant K related to the probability that the two atoms form a molecule? Find an approximate expression for K in terms of the reaction energy E_0, the size r_0 of the molecule, and the width Δr_0 of the potential.

b) Show that the partition function Z_N for N krypton atoms inside a volume V can similarly be written as a sum of contributions coming from M Kr_2 molecules and $N - 2m$ unbound free Kr atoms given by

$$Z_{N,M} = d(M,N) \left(\frac{K}{V}\right)^M Z_N^{id}$$

where Z_N^{id} is the ideal gas partition sum, $d(M,N)$ is the number of ways M molecules can be formed out of N atoms, and K is the same quantity found in part a). Determine the combinatorial factor $d(M,N)$.

c) Derive the equilibrium condition

$$c_{Kr_2} = K[c_{\mathrm{Kr}}]^2$$

where c_{Kr_2} is the concentration of the Kr_2 molecules and c_{Kr} the concentration of the unbound Kr atoms. You may use Stirling's formula $N! \sim \left(\frac{N}{e}\right)^N$.