SMSpring97B

Consider a classical gas of N diatomic molecules in thermal equilibrium with a heat bath at temperature T. The molecules move freely inside a cubic box of volume V. Each molecule consists of two atoms of mass m_1 and m_2 respectively. The two atoms are permanently bound together inside the molecule by intra-molecular forces with potential

$$U(\bar{r}) = U_o\left(\frac{\bar{r}}{a}\right)^{\alpha}$$

where $\bar{r}$ is the relative separation of the two atoms, U_o is a positive constant with units of energy, a is a characteristic length, and α is a positive constant. The molecules do not interact with each other.

Let $j = 1,2,\ldots N$ label the molecules, and for the j^{th} molecule denote by $\bar{R}_j$, $\bar{P}_j$, $\bar{r}_j$, and $\bar{p}_j$ the coordinates of the center of mass, the momentum of the center of mass, the relative separation of its component atoms and their relative momentum. The classical Hamiltonian is

$$E = \sum_{j=1}^{N}\left[+\frac{\bar{p}_j^2}{2\mu}+U(\bar{r}_j)\right]$$

where $M = \frac{1}{2}(m_1 + m_2)$ and $\mu = m_1 m_2/(m_1 + m_2)$.

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(a) Show that the classical partition function Z_N is given by

$$Z_N = A \frac{V^N}{N!}\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3N} \left\{\int_0^\infty 4\pi r^2 e^{-U(r)/k_B T} dr\right\}^N$$

and express the constant A in terms of M and μ.

(b) In the thermodynamic limit $N >> 1$, N/V fixed, calculate the average energy in terms of N, $k_B T$ and α. [Hint: the change of variable $t \equiv U(r)/k_B T$ may be useful. You should not need to evaluate any integrals for this part.]

(c) Calculate the heat capacity at constant volume C_V.

(d) For the case $\alpha = 2$, explain how the answer to (c) could have been obtained without detailed calculation.