

PHYSICS 715

Problem Set 6

Due Friday, March 10, 2006

Reading: Landau and Lifshitz, Secs. 30, 33, 78, 79

LD 18: Thermal properties of rubber – a model.

A simple one-dimensional model of rubber treats the rubber molecule (a long-chain polymer) as a limp chain with n links of length a which can be oriented either to the right (n_+) or to the left (n_-). The separation ℓ between the ends of the folded molecule is $\ell = (n_+ - n_-)a$. Determine the number of ways $\Gamma(n_+, n_-)$ of obtaining a configuration with a given ℓ and show that, when only the average value of ℓ is specified, the appropriate grand partition function for the molecule is

$$\mathcal{Y}(\tau, T) = \sum_{\substack{n_+, n_- \\ n_+ + n_- = n}} \Gamma(n_+, n_-) e^{\beta\tau(n_+ - n_-)a}.$$

τ may be identified as the tension in the chain through the first law, $dG = -SdT - \ell d\tau + \mu dn$ with Gibbs free energy $G = -kT \ln \mathcal{Y}$.

Evaluate the sum above and use the result to determine $\bar{\ell} = \langle \ell \rangle$ as a function of T and τ . Determine the coefficient of thermal expansion $(1/\bar{\ell})(\partial \bar{\ell} / \partial T)_\tau$ and comment on the result.

LD 19: Electric dipole interactions of polar molecules

The dipole interaction between polar diatomic molecules with electric dipole moments \mathbf{p} is given approximately by

$$V_{12}(\mathbf{r}) = \begin{cases} -\frac{1}{r^3} [3(\mathbf{p}_1 \cdot \hat{\mathbf{r}})(\mathbf{p}_2 \cdot \hat{\mathbf{r}}) - (\mathbf{p}_1 \cdot \mathbf{p}_2)], & r > r_0, \\ +\infty, & r < r_0 \end{cases}$$

Here $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ is the relative coordinate giving the separation of the centers of mass of molecules 1 and 2 and $\hat{\mathbf{r}} = \mathbf{r}/r$. The moments \mathbf{p}_i have the same magnitude but may have different orientations. The canonical partition function for the N -particle classical gas confined in a volume V can be reduced to the form

$$Z_N = \frac{Z_{\text{rot}}^N}{N! \lambda^{3N}} \frac{1}{(4\pi)^N} \int d^3r_1 \cdots d^3r_N \int d\Omega_1 \cdots d\Omega_N e^{-\beta \sum_{i < j} V_{ij}(\mathbf{r}_i - \mathbf{r}_j)}$$

where $d\Omega_i = d(\cos \theta)_i d\phi_i$ with θ_i and ϕ_i the polar and azimuthal angles that specify the orientation of \mathbf{p}_i , here averaged over.

Calculate the second virial coefficient for this gas correct to order $(V_{12}/kT)^2$.

LD 20: The Coulomb energy and equation of state of a neutral plasma. Definition and use of the radial distribution function.

The equation of state of a neutral plasma with an average of $N_e/V = N_{\text{ion}}/V = \frac{1}{2}n$ electrons and singly charged positive ions per unit volume is given by the virial theorem as

$$\begin{aligned} P &= nkT + \frac{1}{3} \frac{1}{V} \sum_{i < j} \left\langle \frac{e_i e_j}{|\mathbf{x}_i - \mathbf{x}_j|} \right\rangle \\ &= nkT + \frac{1}{6} nN \left(\left\langle \frac{e^2}{|\mathbf{x}_1 - \mathbf{x}_2|} \right\rangle_{ee} - \left\langle \frac{e^2}{|\mathbf{x}_1 - \mathbf{x}_{N+1}|} \right\rangle_{e-\text{ion}} \right). \end{aligned}$$

The average is over the exact canonical distribution. We have counted the numbers of pairs of each type, hence the factor nN , and have used the identity of the electron-electron and ion-ion distributions to combine the e-e and ion-ion terms. Electrons are labeled $1, \dots, N$, and ions, $N + 1, \dots, 2N$. (See Prob. LD 14.)

- (a) Write out explicitly what $\langle \dots \rangle$ means in terms of integrals involving the potentials, and give an argument to show that P can be written exactly as

$$P = nkT + \frac{1}{6} n \left(\int d^3r \frac{e^2}{r} [n_{ee}(r) - n_{e,\text{ion}}(r)] \right),$$

where $n_{ee}(r)$ and $n_{e,\text{ion}}(r)$ are the radial distributions of electrons and ions relative to a given electron, that is, the numbers of particles per unit volume a distance r from the chosen particle. Give the definition of n_{ee} .

- (b) Evaluate the integrals using the Debye-Hückel expressions for the distribution functions, and determine the temperature dependence of the correction to the ideal gas expression for P .

LD 21: Properties of the quantum density matrix

A quantum system has the probabilities p_i of being in the normalized pure states $|\Psi_i\rangle$, $i = 1, 2, \dots$, with $\sum_i p_i = 1$. The state $|\Psi_i\rangle$ are not necessarily orthogonal, but the Ψ 's can be expanded using a complete orthonormal set of basis states $|\phi_m\rangle$, $|\Psi_i\rangle = \sum_m |\phi_m\rangle c_m^i$ with $c_m^i = \langle \phi_m | \Psi_i \rangle$. The density matrix for this system is $\rho_{mn} = \sum_i p_i c_m^i c_n^{i*}$. Show that the following relations hold.

- (i) $\text{Tr } \rho = 1$.
(ii) $\text{Tr } \rho^2 \leq 1$ with $\text{Tr } \rho^2 = 1$ if and only if ρ describes a pure state.
(iii) $\hat{\rho}$ is a positive Hermitian operator, $\langle \chi | \hat{\rho} | \chi \rangle \geq 0$ for any $|\chi\rangle$, and $\hat{\rho}^\dagger = \hat{\rho}$ where $\hat{\rho}$ is the operator with matrix elements ρ_{mn} .
(iv) $\langle \hat{f} \rangle \equiv \sum_i p_i \langle \Psi_i | \hat{f} | \Psi_i \rangle = \text{Tr } \rho f$ for any observable, where $f_{nm} = \langle \phi_n | \hat{f} | \phi_m \rangle$.
(v) the trace formula in (d) is unchanged by a change in basis $\{\phi_n\} \rightarrow \{\chi_m\}$, that is, $\text{Tr } \rho' f' = \text{Tr } \rho f$ where ρ' , f' are calculated in the new basis.