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 \( \ell \) 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 \( \ell \) and show that, when only the average value of \( \ell \) is specified, the appropriate grand partition function for the molecule is

\[
Y(\tau, T) = \sum_{n_+, n_-} \Gamma(n_+, n_-) e^{\beta \tau (n_+ - n_-)a}.
\]

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

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

\[
V_{12}(\mathbf{r}) = \begin{cases} 
\frac{1}{r} \left[ 3(\mathbf{p}_1 \cdot \hat{\mathbf{r}})(\mathbf{p}_2 \cdot \hat{\mathbf{r}}) - (\mathbf{p}_1 \cdot \mathbf{p}_2) \right], & \text{if } r > r_0; \\
+\infty, & \text{if } r < r_0.
\end{cases}
\]

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

\[
Z_N = \frac{Z_{\text{tot}}^N}{N! \lambda^{3N} (4\pi)^N} \int d^3r_1 \cdots d^3 r_N \int d\Omega_1 \cdots d\Omega_N e^{-\beta \sum_{i<j} V_{ij}(r_i - r_j)}
\]

where \( d\Omega_i = d(\cos \theta_i) d\phi_i \) with \( \theta_i \) and \( \phi_i \) 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

$$P = nkT + \frac{1}{3V} \sum_{i < j} \frac{e_i e_j}{|\mathbf{x}_i - \mathbf{x}_j|}$$

$$= nkT + \frac{1}{6} nN \left( \frac{e^2}{|\mathbf{x}_1 - \mathbf{x}_2|} \langle \frac{e^2}{|\mathbf{x}_1 - \mathbf{x}_{N+1}|} \rangle_{ee} - \langle \frac{e^2}{|\mathbf{x}_1 - \mathbf{x}_{N+1}|} \rangle_{e-\text{ion}} \right).$$

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, $\ldots$, $N$, and ions, $N+1, \ldots, 2N$. (See Prob. LD 14.)

(a) Write out explicitly what $\langle \cdots \rangle$ 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 $|\Psi_i\rangle$, $i = 1, 2, \ldots$, with $\sum_i p_i = 1$. The state $|\Psi_i\rangle$ are not necessarily orthogonal, but the $\Psi$’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 $\rho_{mn} = \sum_i p_i c^m_i c^i_n$. 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 $\rho$ 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 $\rho_{mn}$.

(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 $\rho'$, $f'$ are calculated in the new basis.