

PHYSICS 715

Problem Set 4

Due Friday, February 17, 2006

HOUR EXAM IN CLASS ON WEDNESDAY, FEBRUARY 22

Reading: Landau and Lifshitz, Secs. 26, 32, 34, 35, 37–39

LD 11: Equipartition, anharmonic forces, and the expansion of solids.

The Hamiltonian for a long-chain molecule composed of n distinguishable atoms is

$$H = \sum_{i=1}^n \frac{p_i^2}{2m} + \sum_{i=1}^{n-1} \frac{1}{2} m \omega^2 (q_{i+1} - q_i - a)^2,$$

where q_i , p_i are the position and momentum of the i^{th} atom. The molecule is free to move in a one-dimensional box of length L . Assume that the molecule is very short compared to L , $(n-1)a \ll L$.

- (a) Calculate the partition function Z_N and the specific heat at constant volume

$$C_L = T \left(\frac{\partial S}{\partial T} \right)_L = \left(\frac{\partial E}{\partial T} \right)_L$$

for a classical system of N of these molecules, treated as identical. Compare with the result expected for N free particles plus $(n-1)N$ independent oscillators with frequency ω . Discuss why this result is expected from the equipartition theorem. Hint: do the coordinate integrals successively starting at one end of the chain, or better, change to variables $x_i = q_i - q_{i-1} - a$, $2 \leq i \leq n$, $x_1 = q_1$, before integrating.

- (b) The interaction above is modified for small displacements from equilibrium by a small anharmonic perturbation V' , with $H \rightarrow H' = H + V'$,

$$V' = -c \sum_{i=1}^{n-1} (q_{i+1} - q_i - a)^3, \quad c > 0.$$

Show that the results in part (a) do not change through first order in c . Why is this expected physically? [Hint: expand the factor $e^{-\beta V'}$ in the expression for Z_1 to first order in V' .]

- (c) Calculate the mean length $\ell = \langle q_n - q_1 \rangle$ and the coefficient of thermal expansion $\alpha = \frac{\partial \ell}{\partial T}$ for this molecule (or one-dimensional solid) to first order in c . [Hint: expand the factor $e^{-\beta V'}$ in the expression for ℓ as above. Use the symmetry of the integrand to simplify the result.]

The speed of sound in a solid is $v_s = \omega a$. The speed of sound in tungsten (density 19,300 kg/m³) is $v_s = 5300$ m/s. Use the data on α from 300 to 700 K given in the CRC *Handbook of Chemistry and Physics*, p. E325, to estimate the constant c for tungsten. Give your result in eV/Å³, compare it to the coefficient $\frac{1}{2}m\omega^2$ in the same units, and show that the cubic term is small for reasonable amplitudes of the atomic oscillations.

Explain from the shape of the full potential between particles $i + 1$ and i near equilibrium why $c > 0$ gives thermal expansion, hence, from the normal shape of interatomic potentials, why most solids expand when heated. Why is there no thermal expansion for $c = 0$?

LD 12: Centrifugal isotope separation: equilibrium in a rotating frame.

Natural hydrogen gas contains H₂ and HD in the ratio HD:H₂ = 1:2500. Hydrogen gas at the boiling temperature of liquid nitrogen (77 K) is put in a cylindrical centrifuge with a radius $a = 5$ cm and spun at 60,000 rpm. Determine the maximum degree of enrichment of HD in the centrifuge. Where does it occur? [Hint: Derive the normalized radial distribution functions $\rho(r)$ for HD and H₂ and look at their ratio. Note that $\boldsymbol{\Omega} \cdot \mathbf{L} = \mathbf{p} \cdot \boldsymbol{\Omega} \times \mathbf{r}$ and integrate over \mathbf{p} first. Cylindrical coordinates r, ϕ, z are then useful.]

Assume a continuous flow process with the gas drained off where the HD is most abundant. Estimate the number of stages needed to obtain 90% HD in the output. Centrifugal separation is actually used to separate ²³⁵U from ²³⁸U (natural ratio 7.2×10^{-3}) using the gas UF₆.

LD 13: Noncanonical variables, rotating polar molecules, and the polarizability of gases.

An ideal gas of N polar molecules is subject to a constant electric field of magnitude \mathcal{E}_0 directed along the z axis. The Hamiltonian for a single molecule is

$$H = \frac{\mathbf{p}_{\text{cm}}^2}{2m} + \frac{1}{2I_1}(L_1^2 + L_2^2) + \frac{L_3^2}{2I_3} - p_0 \mathcal{E}_0 \cos \theta$$

where p_0 is the intrinsic dipole moment of the molecule, \mathbf{p}_{cm} is the momentum of the center of mass of the molecule and the L_i are the components of the angular momentum in the body frame. The L 's are *not* canonical momenta, but are related to the Euler angles ϕ, θ, ψ and the corresponding canonical momenta p_ϕ, p_θ, p_ψ by (see Goldstein, *Classical Mechanics*, Chap. 4 and Sec. 9.6))

$$L_1 = p_\theta \cos \psi + (p_\phi - p_\psi \cos \theta) \frac{\sin \psi}{\sin \theta},$$

$$L_2 = -p_\theta \sin \psi + (p_\phi - p_\psi \cos \theta) \frac{\cos \psi}{\sin \theta},$$

$$L_3 = p_\psi.$$

- (a) Determine the Jacobian J in the transformation of the volume element in the rotational phase space to *non-canonical* variables $\phi, \theta, \psi, L_1, L_2, L_3$, i.e.,

$$d\phi d\theta d\psi dp_\phi dp_\theta dp_\psi = J d\phi d\theta d\psi dL_1 dL_2 dL_3.$$

- (b) Calculate the complete canonical partition function for the gas.
- (c) Calculate p , the average electric dipole moment per molecule for the system, defined by

$$p = \gamma \mathcal{E}_0 = \frac{1}{N} \sum_{i=1}^N \langle p_0 \cos \theta_i \rangle.$$

Plot p/p_0 carefully as a function of $x = p_0 \mathcal{E}_0 / kT$, and derive expressions for the limiting behavior of the polarizability γ for $x \sim 0$ and $x \gg 1$. Use reasonable physical assumptions to *estimate* x for the polar molecule HCl in a field of 10^6 V/m at 0°C . Which of the limits above is appropriate?

- (d) The dielectric constant of the gas is given approximately by

$$\epsilon = 1 + 4\pi n\gamma \quad (\text{Gaussian units})$$

where n is the number density of the molecules, $n = N/V$. HCl has a dielectric constant $\epsilon = 1.0046$ at 0°C and 1 atmosphere. Determine p_0 for the HCl molecule from the data given using the appropriate expression from (c). Give your answer in $e\text{-cm}$, where e is the magnitude of the charge of the electron. (This calculation neglects the induced dipole moment of the molecule.) Use the result to estimate the fraction of the electronic charge transferred from the hydrogen atom to the chlorine atom in the ionic binding of the HCl molecule.

Remark: It is customary to use Gaussian, or rationalized Gaussian cgs units in microscopic calculations. Jackson, *Classical Electrodynamics*, gives the relations necessary to convert between Gaussian cgs and SI units for electromagnetic quantities in the Appendix on Units, Sec. 4, Table 3. Check that the expression for x above is invariant. The result for p_0 in terms of ϵ is not!