NATIONAL TECHNICAL UNIVERSITY OF ATHENS
INTERDEPARTMENTAL GRADUATE PROGRAMMES: MATHEMATICAL
MODELLING IN MODERN TECHNOLOGIES AND FINANCIAL ENGINEERING,
MICROSYSTEMS AND NANODEVICES,
COMPUTATIONAL MECHANICS,
MATERIALS SCIENCE AND TECHNOLOGY

MOLECULAR SIMULATIONS OF MATERIALS

Spring Semester 2026

Problem Set 1

due Monday, 6 April 2026

Problem 1: Ergodicity of a one-dimensional harmonic oscillator

For a classical, one-dimensional harmonic oscillator of total energy E, governed by the Hamiltonian $\mathcal{H}(p, q) = \dfrac{p^2}{2m} + \dfrac{k}{2} q^2$, prove that the phase average $\langle \mathcal{A} \rangle_\Sigma$ of any configuration-dependent quantity $\mathcal{A}(q)$ coincides with the time average $\langle \mathcal{A} \rangle_t$ along a trajectory.

Hint: The constant energy hypersurface for this system is a closed line on the pq plane. This line can be viewed as an infinitesimally thin two- dimensional band corresponding to energies between $E - \delta E$ and E. To calculate an integral over this band, it is convenient to first calculate the integral over the two-dimensional domain $\mathcal{H}(p, q) < E$ and then take the differential of the result with respect to E.

Problem 2: Gibbs entropy formula

(a) A remarkable connection exists between the equilibrium probability distribution of microstates and the entropy of a system:

$$S = -k_B \sum_{\nu} P_\nu^{eq} \ln P_\nu^{eq} = -k_B \left\langle \ln P_\nu^{eq} \right\rangle_{eq} \qquad (H2.1)$$

In Eq. (H2.1), known as *Gibbs entropy formula*, the summation is taken over all microstates constituting the phase space of the system. P_ν^{eq} is the probability of microstate ν, as dictated by an equilibrium ensemble under given external constraints, and $\langle\ \rangle_{eq}$ denotes averaging over all microstates with respect to the probability distribution $\{P_\nu^{eq}\}$. Eq. (H2.1) holds *in any ensemble*!

Prove the validity of Eq. (H2.1) in the microcanonical, canonical, isothermal-isobaric, and grand canonical ensembles.

(b) In an alternative formulation to the one we presented in class, one can derive thermodynamics by introducing as fundamental postulates the Gibbs entropy formula and a variational statement of the second law. In other words, one can deduce the entire formalism of ensembles by introducing the following axiom:

Let ν symbolize the microstates accessible to a system in a given macroscopic state, and P_ν the probability that the system finds itself in microstate ν. At thermodynamic equilibrium, the system will assume that probability distribution $\{P_\nu^{eq}\}$ among microstates which maximizes the function

$$\mathcal{S}\left(\{P_\nu\}\right) = -k_B \sum_\nu P_\nu \ln P_\nu \qquad (H2.2)$$

under a set of constraints such that $\{P_\nu^{eq}\}$ is *consistent with the macroscopic state* of the system. Furthermore, the entropy of the system at equilibrium is related to the maximal value of the function $\mathcal{S}\left(\{P_\nu\}\right)$ by Eq. (H2.1).

The phrase "under a set of constraints, such that $\{P_\nu^{eq}\}$ is consistent with the macroscopic state of the system" requires some explanation. First, the normalization constraint

$$\sum_\nu P_\nu = 1 \tag{H2.3}$$

must be satisfied. In addition, for any extensive property X that is allowed to fluctuate, the average

$$\langle X \rangle \equiv \sum_\nu X_\nu \, P_\nu \tag{H2.4}$$

must be fixed and equal to the value of X characteristic of the macroscopic (thermodynamic) state of the system. Thus, in the canonical ensemble (energy fluctuating) we must require Eq. (H2.4) with $X = E$; in the isothermal-isobaric ensemble (energy and volume fluctuating) we must require Eq. (H2.4) with $X = E$ and $X = V$; in the grand canonical ensemble (energy and number of particles fluctuating) we must require Eq. (H2.4) with $X = E$ and $X = N$. Note that if, instead of a discrete representation, we use a continuum of microstates (continuous phase space), $\mathcal{S}$, as defined by Eq. (H2.2), becomes a *functional* of the probability density distribution of microstates.

Using a discrete representation of microstates, and applying the maximization principle, Eq. (H2.2), under the constraints (H2.3) and (H2.4) appropriate for the *canonical ensemble*, derive the Boltzmann probability distribution $\{P_\nu^{eq}\}$. You may use the method of Lagrange multipliers in your constrained optimization.

Problem 3: Thermodynamics of a system of noninteracting spins in a field

Consider a lattice with L equivalent magnetic dipoles, μ (associated, say, with electron or nuclear spins) that don't interact with each other. When placed in a magnetic field H, each dipole can orient itself either in the same direction, ↑, or opposed to, ↓, the field. The energy of a dipole is $-\mu H$ if it is oriented with the field, and $+\mu H$ if it is oriented against the field. Let N be the number of ↓ dipoles and $L - N$ the number of ↑ dipoles; both these numbers fluctuate as the system changes configuration. For a given configuration, the energy is

$$\mu H N - \mu H(L-N) = (2N-L)\mu H \qquad (H2.5)$$

The *magnetization* M is an extensive thermodynamic property, defined as

$$M = \text{ average total magnetic moment } =$$

$$\mu(\text{average number of } \uparrow \text{ spins} - \text{average number of } \downarrow \text{ spins}) =$$

$$\mu\left\{(L - \langle N\rangle) - \langle N\rangle\right\} = (L - 2\langle N\rangle)\,\mu \qquad (H2.6)$$

where $<N>$ denotes an ensemble average of N at given L, H, and T.

By formulating the statistical mechanics of this system in the constant L, H, T ensemble, derive an expression for the magnetization M and for the heat capacity (temperature derivative of the thermodynamic energy at constant field) C. Sketch $\dfrac{M}{L\,\mu}$ *versus* $\dfrac{\mu\,H}{k_B\,T}$ and $\dfrac{C}{L\,k_B}$ *versus* $\dfrac{k_B\,T}{\mu\,H}$.

Problem 4: Alternative derivation of the virial theorem

In class we discussed the Clausius derivation of the virial theorem, which is based on kinetic theory arguments. The same expression for pressure in terms of temperature, density, and the ensemble average of a mechanical quantity (the virial) that depends on molecular positions and intermolecular forces can be derived from the formalism of the canonical ensemble by introducing a simple scaling transformation of molecular coordinates. You are asked to develop this derivation here.

Start from the definition of the configurational integral for N molecules in a *cubic* domain of volume V at temperature T, subject to a total potential energy $\mathcal{V}(\mathbf{r}_1, \ldots, \mathbf{r}_N)$:

$$Z(N,V,T) = \int_{\substack{\text{all configuration} \\ \text{space}}} exp\left[\frac{-1}{k_B\,T}\,\mathcal{V}(\mathbf{r}_1, \ldots, \mathbf{r}_N)\right] d^3r_1\, d^3r_2\, \ldots\, d^3r_N \qquad (H2.7)$$

Now, in place of the Cartesian coordinates $(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ introduce the (dimensionless) *scaled* coordinates $(\mathbf{s}_1, \mathbf{s}_2, \ldots, \mathbf{s}_N)$, defined as

$$\mathbf{s}_i = V^{-1/3}\,\mathbf{r}_i \qquad (i = 1, 2, \ldots, N) \qquad (H2.8)$$

If our Cartesian coordinate system is chosen so that the cubic domain of fluid lies entirely within the first quadrant (positive x, y, z) with one apex at the origin $(0,0,0)$, then each component of the three-dimensional vectors $\mathbf{s}_i$ lies between 0 and 1. Express Z as an integral over this scaled coordinate space.

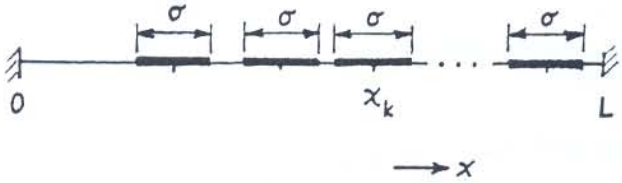
By invoking the relation between pressure and configurational integral, show that straightforward differentiation leads to the virial theorem

$$p = \rho\, k_B\, T + \frac{1}{3\,V}\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i^{int} \right\rangle \qquad (H2.9)$$

where $\rho = N/V$ is the molecular density, and $\mathbf{F}_i^{int}$ is the total force on molecule i due to its interactions with other molecules.

Problem 5: Equation of state of a one-dimensional gas of hard molecules

We have pointed out that an exact derivation of the equation of state for a three-dimensional gas of hard spheres is impossible. Interestingly, an exact equation of state can be derived for a one- dimensional gas of hard molecules constrained to move on a line between two points. This was first pointed out by Lewi Tonks at General Electric in 1936, hence the name *Tonks gas* for a one-dimensional gas of hard molecules ("hard rods").



Consider a set of N molecules of diameter (length) σ, constrained to move along a line between two fixed impenetrable boundaries placed at a distance L from each other. The intermolecular potential is perfectly hard, *i.e.*, the intermolecular energy is infinite for any configuration in which there is at least one pair of molecular centers at a distance less than σ from each other, and zero otherwise. Likewise, molecule-boundary interactions are perfectly hard, *i.e.*, the total energy is infinite if a molecular center comes closer than $\sigma/2$ to one of the two boundaries. The configuration space of this system is clearly N-dimensional, spanned by the molecular center coordinates $x_k,\ k = 1(1)N$. "Volume" in such a system reduces to the length L.

(a) Show that the configurational integral of the Tonks gas can be obtained exactly as

$$Z(N, L, T) = (L - N\sigma)^N \qquad (H2.10)$$

Hint: A configuration contributes to Z if

$$\sigma/2 \leq x_k \leq L - \sigma/2,\ |x_k - x_j| \geq \sigma \text{ for all molecules } j, k$$

Whatever sequence the molecules are in remains fixed for all time, as molecules cannot pass through each other; there is a large number of possible sequences, however.

(b) Derive the equation of state of the Tonks gas.

Note: "Pressure" for this one-dimensional system has the meaning of an average *force* exerted at either boundary.

Problem 6: Heat capacity of ideal diatomic gas

We have mentioned in section 4.7 that the thermodynamic properties of a fluid in the ideal has state depend on the internal partition function $q^{int}(T)$, which incorporates contributions to the energy from nuclear, electronic, vibrational, rotational, and torsional degrees of freedom. The separation of successive energy levels associated with nuclear and electronic degrees of freedom is typically very large compared to $k_B\, T$. Thus, at ordinary temperatures these degrees of freedom occupy almost exclusively their ground states, which means that they contribute just a constant (temperature-independent) factor to q^{int}. Our objective here is to explore the effects of vibrational and rotational degrees of freedom on the thermodynamics of an ideal diatomic gas.

A diatomic molecule has one vibrational degree of freedom. The amplitude of vibrations is quite small. Thus, it is reasonable to consider all motion of the molecule relative to its center of mass as consisting of two independent contributions: Vibration of the bond, and rotation of a rigid dumbbell at fixed internuclear distance. Furthermore, for small amplitude oscillations around the equilibrium bond length, the anharmonic characteristics of the bond potential can be neglected (i.e., the bond potential can be viewed as a strictly quadratic function of intermolecular separation). This constitutes the *rigid rotor-harmonic oscillator* approximation. In this approximation, for one molecule,

$$E^{int} = E^{rot} + E^{vib} \qquad (H2.14)$$

where vibrational and rotational quantum states are populated independently, and

$$q^{int} = q^{rot}\, q^{vib} \qquad (H2.15)$$

A solution of the Schrödinger equation for a rigid rotor consisting of masses m_1 and m_2 at an equilibrium separation r_e gives the following results:

Eigenvalues (energy levels): $$E_J^{rot} = \frac{h^2\, J\,(J+1)}{8\,\pi^2\, I} \quad (J = 0, 1, 2, \ldots) \tag{H2.16}$$

Degeneracy: $2J + 1$ for each J

(*i.e.*, there are $2J + 1$ rotational microstates with energy E_J^{rot}.) The quantity $I = \frac{m_1\, m_2}{m_1 + m_2}\, r_e^2$ is the moment of inertia of the rigid rotor.

The rotational partition function becomes

$$q^{rot}(T) = \sum_{J=0}^{\infty} (2J+1)\; exp\left[-\beta \frac{h^2}{8\,\pi^2\, I}\, J\,(J+1)\right] =$$

$$\sum_{J=0}^{\infty} (2J+1)\; exp\left[-\frac{\Theta_r}{T}\, J\,(J+1)\right] \tag{H2.17}$$

where $\Theta_r = \frac{h^2}{8\,\pi^2\, I\, k_B}$, characteristic temperature of rotation.

The quantity $\frac{\Theta_r}{T}$ is quite small at ordinary temperatures for most molecules. Application of the Euler-Maclaurin summation formula to the partition function, Eq. (H2.17), gives

$$q^{rot}(T) = \frac{T}{\Theta_r}\, \left\{1 + \frac{1}{3}\left(\frac{\Theta_r}{T}\right) + \frac{1}{15}\left(\frac{\Theta_r}{T}\right)^2 + \cdots\right\} \tag{H2.18}$$

A solution of the Schrödinger equation for a harmonic oscillator consisting of masses m_1 and m_2 (reduced mass $\frac{m_1\, m_2}{m_1 + m_2}$) kept together with a harmonic potential of spring constant k leads to the following results:

Eigenvalues (energy levels): $E_n^{vib} = h\,\nu \left(n + \frac{1}{2}\right) \quad (n = 0, 1, 2, \ldots)$

$(H2.19)$

Degeneracy: 1 for each n

where the characteristic frequency ν is given by

$$\nu = \frac{1}{2\pi}\left[\frac{k}{m_1\,m_2}(m_1 + m_2)\right]^{\frac{1}{2}} \tag{H2.20}$$

(a) Show that the vibrational partition function for a diatomic molecule can be written as

$$q^{vib}(T) = \frac{e^{-\frac{\Theta_v}{2T}}}{1 - e^{-\frac{\Theta_v}{T}}} \tag{H2.21}$$

where $\Theta_v = \dfrac{h\,\nu}{k_B}$ is a characteristic temperature of vibration.

(b) On the basis of the above analysis of $q^{int}(T)$, show that the heat capacity of a heteronuclear diatomic gas at constant pressure is given by

$$\frac{c_P^{ig}}{R} = \frac{7}{2} + \left(\frac{\Theta_v}{T}\right)^2 \frac{e^{-\frac{\Theta_v}{T}}}{\left(1 - e^{-\frac{\Theta_v}{T}}\right)^2} + \frac{1}{45}\left(\frac{\Theta_r}{T}\right)^2 + \cdots \tag{H2.22}$$

(c) Predict the heat capacity c_P^{ig} for HCl at $400K$. The equilibrium length of the H-Cl bond can be taken as 1.29 Å, and the force constant k as 4.9×10^5 dyn/cm. The atomic weights of H and Cl can be taken as 1 g/mol and 35.5 g/mol, respectively. How does your estimate compare with the experimental value, 6.96 cal $\text{mol}^{-1}\text{K}^{-1}$ at the considered temperature?