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

MOLECULAR SIMULATIONS OF MATERIALS

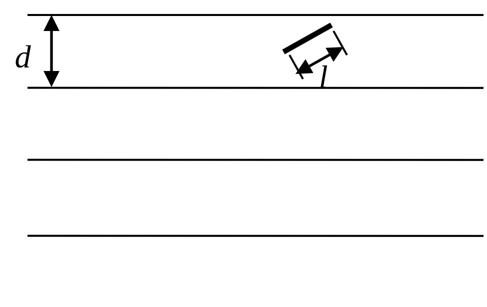
Spring Semester 2026

Problem Set 2

due Monday, 18 May 2026

Problem 1 (20 points) **Proof of Buffon's Theorem**

This exercise is designed to refresh your memory of calculations involving multivariate distribution functions. You are asked to prove the theorem introduced in 1777 by Georges-Louis Leclerc, Comte de Buffon:



A needle of length l is thrown randomly onto a large set of equally spaced parallel lines. The spacing between the lines is d, where $d > l$. Prove that the probability that the needle will cross a line is $\frac{2l}{\pi d}$.

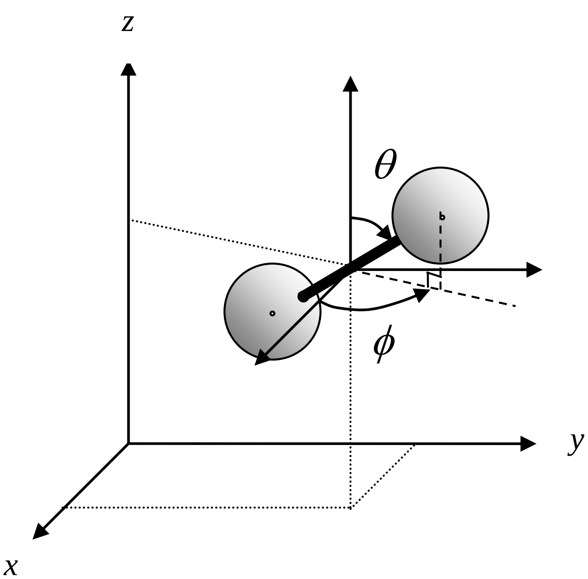
Hint: It is convenient to cast the configuration space of the needle in terms of two variables: the coordinate z of the needle center, measured on an axis perpendicular to the parallel lines, and a rotation angle θ of the needle relative to the lines. Express the probability density $\rho(z,\theta)$ in terms of these coordinates. Express the mathematical condition between z and θ that has to be satisfied for a crossing to occur. Find the sought probability as an integral of the probability density over all regions in configuration space that correspond to a crossing.

Problem 2 (12 points) **Monte Carlo Sampling of Molecular Orientations**

In Monte Carlo simulations of rigid polyatomic molecules, attempts to change the overall orientation of molecules must be used in addition to random displacements in order to sample configuration space.

Consider the case of *NVT* Monte Carlo of liquid bromine, represented as a system of rigid diatomic molecules. Bromine atoms on different molecules are assumed to interact via a pairwise additive Lennard-Jones potential. The configuration of a bromine molecule is described in terms of five degrees of freedom: three center of mass coordinates **r** and two polar angles θ, ϕ specifying the orientation of the Br-Br bond (see Figure). Elementary moves consist of random displacements of centers of mass, each component of the displacement being uniformly distributed in the interval $(-\delta r_{max}, \delta r_{max})$; also, of random changes in the two orientation angles, chosen from two uniform distributions within the intervals $(-\delta\theta_{max}, \delta\theta_{max})$ and $(-\delta\phi_{max}, \delta\phi_{max})$.

Definition of the 5 degrees of freedom of the bromine molecule, $(\underbrace{x, y, z}_{\mathbf{r}}, \theta, \phi)$



Construct a simple flow sheet outlining the calculations taking place in a Monte Carlo step. Pay particular attention to the Metropolis selection criteria associated with the reorientation moves. Generations of pseudorandom numbers should be shown explicitly in your flow sheet.

Problem 3 (20 points) **Calculation of a Sorption Isotherm by GCMC**

a. (5 points) In class we discussed briefly the Grand Canonical Monte Carlo method, designed to simulate a phase under given temperature, spatial extent, and chemical potentials of all species present in it. Explain why this method is particularly convenient as a means of predicting sorption equilibria on solid surfaces or in microporous solids.

b. (8 points) Consider the adsorption of pure gaseous methane in a zeolite. You have been given a detailed microscopic model of the zeolite crystal, consisting of oxygen, silicon, aluminum, and counterion centers at their crystallographically correct positions. Pores of diameter roughly 0.55 nm are present within the zeolite, in which methane can sorb from the gas phase. Our computer model of the zeolite consists of a collection of unit cells, occupying total volume V_s in space. It is characterized by periodic boundary conditions in all three directions; thus, it can be envisioned as part of an infinite (macroscopic) zeolite crystal. In this problem it is reasonable to represent methane molecules as Lennard-Jones spheres. An expression for the methane-methane pairwise interaction potential $\upsilon(r)$ that is safe to use within the zeolite phase is available as a function of the intermolecular distance r. You have also computed and pretabulated the potential $\mathcal{V}_s(\mathbf{r})$ that a methane molecule experiences at every point $\mathbf{r}$ within the micropores as a result of its interactions with the zeolite framework and counterions.

An accurate equation of state is available for methane in the gas phase. This equation of state provides the compressibility factor $Z(T,P)=(PV_m)/(RT)$ of gaseous methane as a function of temperature T and pressure P, with V_m being the gas-phase molar volume.

Your task is to predict the sorption isotherm of methane in the zeolite based on a series of Grand Canonical Monte Carlo simulations of the adsorbed methane phase in the zeolite.

Express the parameter B invoked in Adams's formulation of GCMC in terms of the fugacity of methane in the gas phase. Show that B can be calculated immediately given the temperature and the gas-phase pressure.

c. (7 points) Outline a computational strategy for predicting the sorption isotherm at temperature T over a wide range of pressures. What are the moves you will use in the GCMC simulations you will conduct, and what are the Metropolis selection criteria for each type of move?

By sorption isotherm we mean a plot or functional relation between the amount of fluid sorbed at equilibrium within the microporous solid (molecules of methane sorbed per unit volume zeolite), and pressure in the gas phase at given temperature.

Problem 4 (18 points) **Nosé-Hoover extended system methods for NVT-MD**

In class we discussed Nosé's extended system method for carrying out molecular dynamics simulations in the canonical ensemble. The dynamical equations, derived from the extended system Lagrangian, are:

$$\ddot{\mathbf{r}}_i = \frac{\mathbf{f}_i}{m_i s^2} - 2\frac{\dot{s}\dot{\mathbf{r}}_i}{s} \quad \text{(P4.1)}$$

$$Q\ddot{s} = \sum_i m_i s \dot{\mathbf{r}}_i^2 - (f+1)\frac{k_B}{s}T_{eq} \quad \text{(P4.2)}$$

where $\mathbf{r}_i$ stands for the coordinate vector of atom i, $\mathbf{f}_i$ is the total force acting on atom i, s is the extra degree of freedom representing the heat bath, f is the total number of degrees of freedom of the system (not counting s), T_{eq} is the bath temperature, m_i is the mass of atom i and Q is the inertial parameter associated with fluctuations in s. Dots above symbols denote derivatives with respect to *simulation time* (not real time).

From the Lagrangian formulation, one immediately concludes that the quantity

$$\mathcal{H}' = \frac{1}{2}\sum_i m_i s^2 \dot{\mathbf{r}}_i^2 + \frac{1}{2}Q\dot{s}^2 + \mathcal{V}(\mathbf{r}) + (f+1)k_{\mathrm{B}}T_{\mathrm{eq}} \ln s \qquad \text{(P4.3)}$$

is a conserved quantity of the simulation, i.e., $\mathcal{H}' = E'$=const. during the simulation.

Again from the Lagrangian formulation for the extended system, the generalized momenta associated with $\mathbf{r}_i$ and s are defined as

$$\mathbf{p}_i = m_i s^2 \dot{\mathbf{r}}_i \qquad \text{(P4.4)}$$

$$p_s = Q\dot{s} \qquad \text{(P4.5)}$$

Note that $\mathbf{p}_i$ is not the actual momentum of atom i (i.e., it does not coincide with the product of its mass times its velocity based on real time).

a. (7 points) In a manner entirely analogous to that used in formulating the microcanonical ensemble, the partition function of the extended system can be shown to be:

$$Q_{NVE'} = \frac{1}{N!h^{f+1}} \int dp_s \int d^f p \int ds \int d^f r \;\delta\left(\sum_i \frac{\mathbf{p}_i^2}{2m_i s^2} + \frac{p_s^2}{2Q} + \mathcal{V}(\mathbf{r}) + (f+1)k_{\mathrm{B}}T_{\mathrm{eq}} \ln s - E' \right) \qquad \text{(P4.6)}$$

where the delta function within the integral expresses the constancy of $\mathcal{H}'$, defined by eq (P4.3).

Show that the partition function $Q_{NVE'}$ can be written as

$$Q_{NVE'} = \frac{1}{(f+1)h}\left(\frac{2\pi Q}{k_{\mathrm{B}}T_{\mathrm{eq}}}\right)^{1/2} \exp\left(\frac{E'}{k_{\mathrm{B}}T_{\mathrm{eq}}}\right) \frac{1}{N!h^f} \int d^f p' \int d^f r \;\exp\left[-\mathcal{H}(\mathbf{p}',\mathbf{r})\frac{1}{k_{\mathrm{B}}T_{\mathrm{eq}}}\right] \qquad \text{(P4.7)}$$

where $\mathcal{H}(\mathbf{p}',\mathbf{r})$ is the Hamiltonian if the original system and

$$\mathbf{p}_i' = \frac{\mathbf{p}_i}{s} = m_i s \dot{\mathbf{r}}_i \qquad \text{(P4.8)}$$

What is the physical meaning of $\mathbf{p}'$, and why?

On the basis of eq (P4.7) show that the Nosé MD method samples the phase space of the original system according to the probability distribution of the canonical ensemble at temperature T_{eq}.

c.(4 points) If the instantaneous temperature of the original system is defined by

$$\frac{f}{2} k_{\text{B}} \mathcal{T} = \sum_i \frac{(\mathbf{p}_i')^2}{2m_i} = \sum_i \frac{\mathbf{p}_i^2}{2m_i s^2} \qquad \text{(P4.9)}$$

show that $\langle \mathcal{T} \rangle = T_{\text{eq}}$ (P4.10)

where angular brackets stand for ensemble averages computed in the course of the extended system MD simulation.

c. (7 points) The disparity between simulation time and real time characteristic of the original Nosé algorithm is inconvenient. Show that, by taking into account the relationship

$$dt_{\text{real}} = dt_{\text{simulation}} \frac{1}{s} \qquad \text{(P4.11)}$$

and using f in place of (f+1) in eq (P4.2), the dynamical equations of Nosé can be cast into the form

$$\mathbf{p}_i' = m \frac{d}{dt_{\text{real}}} \mathbf{r}_i \qquad \text{(P4.12)}$$

$$\frac{d}{dt_{\text{real}}} \mathbf{p}_i' = \mathbf{f}_i - \zeta \mathbf{p}_i' \qquad \text{(P4.13)}$$

$$\frac{d}{dt_{\text{real}}} \zeta = \left(\sum_i \frac{(\mathbf{p}_i')^2}{m_i} - f k_{\text{B}} T_{\text{eq}} \right) \frac{1}{Q} \qquad \text{(P4.14)}$$

where ζ is an appropriately defined quantity.

How do you justify the term "thermodynamic friction coefficient" that has been coined for ζ?

Equations (P4.12) to (P4.14) constitute the Hoover formulation for *NVT* molecular dynamics, which is cast in real time. They can be shown to lead to a stationary phase-space probability density that conforms to the canonical ensemble for the system of interest.

Mathematical note:

For a differentiable function $g(s)$ having one real zero, $\delta(g(s)) = \dfrac{\delta(s-s_0)}{g'(s)}$,

where s_0 is the zero of $g(s)=0$ and $g'(s) = \dfrac{dg}{ds}$.

Problem 5 (15 points) **Interdiffusion Coefficient in Equilibrium Binary System**

In class we discussed the Green-Kubo relation for obtaining the interdiffusion coefficient D in a binary mixture of simple liquids at equilibrium:

$$D = \frac{1}{3}\left(\frac{\partial^2(\beta G/N)}{\partial x_1^2}\right)_{P,T} \frac{1}{N}\int_0^\infty \left\langle \mathbf{j}^{\mathrm{c}}(t)\cdot\mathbf{j}^{\mathrm{c}}(0)\right\rangle dt \qquad \text{(P5.1)}$$

where

G = total Gibbs energy (extensive thermodynamic property)
N = total number of molecules of both species; $N=N_1+N_2$
x_ν = mole fraction of species ν (ν = 1, 2); $x_\nu = N_\nu/N$
$\mathbf{j}^{\mathrm{c}}(t)$ = microscopic interdiffusion current:

$$\mathbf{j}^{\mathrm{c}}(t) = x_2\mathbf{j}^1(t) - x_1\mathbf{j}^2(t) \qquad \text{(P5.2)}$$

$$\mathbf{j}^{\nu}(t) = \sum_{i=1}^{N_\nu}\mathbf{u}_i(t) \equiv N_\nu\mathbf{u}_{\mathrm{cm},\nu} \qquad \text{(P5.3)}$$

with $\mathbf{u}_i$ = velocity vector of molecule i
$\mathbf{u}_{\mathrm{cm},\nu}$ = velocity of center of mass of molecules of type ν.

a. (6 points) Write the Einstein relation corresponding to eq (P5.1).
It is most convenient for computations to cast the Einstein equation in terms of the displacements of the centers of mass of species 1 and 2.

b. (9 points) Many mixtures of simple liquids are nearly ideal. In addition, cross-correlations between the velocities of different molecules of the type $\left\langle \mathbf{u}_i(t)\cdot\mathbf{u}_j(0)\right\rangle$ $(i \neq j)$ can be assumed negligible for all t.

Show that, under these conditions (ideal mixture behavior, negligible cross-correlations between molecular velocities), the interdiffusion coefficient can be found from the self-diffusion coefficients of species 1 and 2 in the mixture as

$$D^{\mathrm{id}} = x_2 D_{s,1} + x_1 D_{s,2} \qquad \text{(P5.4)}$$

Problem 6 (15 points) **Estimation of free energy differences by Monte Carlo**

a. (7 points) We have seen that *NVT* Metropolis Monte Carlo simulations are designed to compute averages with respect to the probability density $\rho^{NVT}(\mathbf{r})$ of the canonical ensemble in configuration space. We have also pointed out that calculating free energy quantities by molecular simulation is more difficult than calculating "mechanical" quantities, such as energy or pressure. In this problem we wish to briefly explore this question of calculating free energies.

Show that the excess Helmholtz energy of a classical system can be written as

$$A^{\mathrm{ex}}(N,V,T) = A(N,V,T) - A^{\mathrm{ig}}(N,V,T) = k_{\mathrm{B}}T \ln\left\langle \exp(\beta\mathcal{V})\right\rangle_{NVT} \quad \text{(P6.1)}$$

where the brackets indicate averaging with respect to the probability density
$\rho^{NVT}(\mathbf{r}) = \dfrac{1}{Z(N,V,T)} \exp\left[-\beta\mathcal{V}(\mathbf{r})\right]$
and $\mathcal{V}(\mathbf{r})$, $Z(N,V,T)$ are the potential energy function and the configurational integral, respectively. The argument on the right-hand side of eq (P6.1) has the form of an ensemble average. In principle, it could be computed by *NVT* Monte Carlo. Such an approach, however, is never used in practice. Why?

b. (8 points) Consider two systems, 0 and 1, with the same number of degrees of freedom, governed by potential energy functions $\mathcal{V}_0(\mathbf{r})$ and $\mathcal{V}_1(\mathbf{r})$, respectively.
Let $\rho_1^{NVT}(\mathbf{r}) = \dfrac{1}{Z_1(N,V,T)} \exp\left[-\beta\mathcal{V}_1(\mathbf{r})\right]$ and $\rho_0^{NVT}(\mathbf{r}) = \dfrac{1}{Z_0(N,V,T)} \exp\left[-\beta\mathcal{V}_0(\mathbf{r})\right]$.
Show that the *difference* in Helmholtz energy between the two systems can be expressed as

$$A_1(N,V,T) - A_0(N,V,T) = -k_{\mathrm{B}}T \ln\left\langle \exp(-\beta\Delta\mathcal{V})\right\rangle_0 \qquad \text{(P6.2)}$$

where $\Delta\mathcal{V}(\mathbf{r}) = \mathcal{V}_1(\mathbf{r}) - \mathcal{V}_0(\mathbf{r})$ and the ensemble average $\langle\ \rangle_0$ is taken with respect to the probability density ρ_0^{NVT}.

If one knows the free energy of the reference system 0, one can use eq (P6.2) to calculate the free energy of system 1. For example, 0 may be a hard sphere fluid, for which A_0 can be calculated directly from the Carnahan-Starling equation of state, while 1 may be a Lennard-Jones fluid with similar collision diameter but exhibiting weak attractive interactions. Equation (P6.2) is practically very useful; it forms the basis of “free energy perturbation” simulation methods and is frequently combined with “umbrella sampling” techniques for enhancing the efficiency of averaging.

Describe in a few words how you would use an *NVT* Monte Carlo simulation to compute A_1-A_0 based on eq (P6.2). What condition must be fulfilled by the systems 0 and 1 for your estimate to be safe?