Statistical Physics and Computer Simulations
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Final Exam

Instructions

1. Relax.
2. Relax.
3. Relax.
4. Read all problems carefully. Take your time, and ask yourself how this relates to what you have learned in the lectures and tutorials.
5. Do not be scared off by the length of the problem texts. Most of it is just to explain precisely the background. In my opinion, the problems are much easier than they look at first glance.
6. Pick your two favourite problems, and solve them *and only them*. If you turn in more than the solutions of two problems, only those two problems will be counted in which you have performed best.
7. I consider all six problems as equally difficult (or easy — as you prefer). We count *one* problem as 100%, and that is sufficient to pass (which in turn means that two half–solved problems are sufficient as well).
8. If you have questions, do not hesitate to ask!
9. Allotted time: At least three hours.

I wish you lots of success!

Problems

1. **One–Dimensional Brownian Motion in a Harmonic Potential**
   Consider a Brownian particle with coordinate x in a harmonic potential $U(x) = (k/2)x^2$. The force acting on the particle is $F = -\partial U/\partial x = -kx$, its mobility is denoted by μ, and its diffusion constant is $D = k_B T \mu$, where k_B is Boltzmann's constant and T is the temperature (Einstein relation). The Langevin equation for the particle motion is

   $$\frac{d}{dt}x = \mu F + f, \tag{1}$$

   where f is a Gaussian white noise with

   $$\langle f(t) \rangle = 0 \qquad\qquad \langle f(t) f(t') \rangle = 2D\delta\left(t - t'\right). \tag{2}$$

   Find the exact solution of the Fokker–Planck equation for the conditional probability density $P(x, t|x_0, 0)$. Use this solution to construct a suitable Brownian dynamics algorithm that updates the coordinates without a discretization error in time. Show explicitly that this procedure satisfies the detailed–balance condition.

2. **The Constant–Pressure Ensemble Revisited**
In exercise sheet 4 we discussed the constant–pressure (NpT) ensemble, and showed that it is described by the partition function

$$Z = \int_0^\infty dV \int d\Gamma_V \exp\left(-\beta\mathcal{H} - \beta pV\right), \tag{3}$$

where V is the (fluctuating) volume of the system, Γ_V is the set of all phase space variables, β is the inverse temperature, $\mathcal{H}$ is the Hamiltonian of the N–particle system, and p is the pressure. We assume a three–dimensional system in a periodic box of size $V = L \times L \times L$. In the integration over the phase space, we take into account that the volume is fixed (i. e. given by the external integration), such that the coordinates are restricted to the box. $\mathcal{H}$ depends on the volume, due to the interactions with the periodic images. Uninteresting prefactors have been omitted in Z. We also showed that the Gibbs free enthalpy $G = E - TS + pV$ is given by

$$-\beta G = \ln Z. \tag{4}$$

(a) The isothermal compressibility is given by

$$\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_T. \tag{5}$$

Show that this is proportional to the mean square fluctuations of the volume.

(b) A Monte Carlo simulation in the constant–pressure ensemble is done as follows: At fixed volume (i. e. fixed box size L) one performs some standard Metropolis updates as they are known from the (NVT) ensemble. Every few Monte Carlo steps (say, every tenth, for the sake of concreteness) one does a volume update as follows:

- One introduces reduced coordinates $\vec{s}_i$, such that the particle coordinates $\vec{r}_i$ are given by $\vec{r}_i = L\vec{s}_i$.
- One generates a trial box size L' by choosing randomly (using a uniform distribution) some value from the interval $(L - \Delta L, L + \Delta L)$, where ΔL is some fixed simulation parameter. One uses this L' together with the unchanged set of *reduced* coordinates $\vec{s}_i$ as a trial configuration.
- One calculates an *effective* energy change $\Delta E_{eff} = \mathcal{H}_{eff}(L') - \mathcal{H}_{eff}(L)$ for some effective Hamiltonian $\mathcal{H}_{eff}$ that may depend not only on the volume, but also on temperature and pressure. One uses this value ΔE_{eff} for a standard Metropolis procedure.

Your task is to find the effective Hamiltonian. Give a formal reason why any generated trial configuration that has $L' \leq 0$ must be rejected.

3. **The Nose–Hoover Thermostat**
Consider a system of N particles in three–dimensional space, in a box of size $V = L\times L\times L$ with periodic boundary conditions. Particle coordinates and momenta are denoted by $\vec{r}_i$ and $\vec{p}_i$, respectively. All particles have the same mass m, and the force on particle i (resulting from the interparticle potential U) is denoted by $\vec{F}_i = -\partial U/\partial\vec{r}_i$. This system is (artificially) coupled to *one* additional degree of freedom $\zeta(t)$ via the following *deterministic* equations of motion

$$\frac{d}{dt}\vec{r}_i = \frac{1}{m}\vec{p}_i, \tag{6}$$

$$\frac{d}{dt}\vec{p}_i = \vec{F}_i - \zeta\vec{p}_i, \tag{7}$$

$$\frac{Q}{2}\frac{d}{dt}\zeta = \frac{1}{2m}\sum_i \vec{p}_i^{\,2} - \frac{3}{2}Nk_BT. \tag{8}$$

During the dynamic evolution of the system, ζ takes both positive and negative values — it should not be confused with a friction constant! Q is a "mass"–like parameter that can be chosen at will. Your task is to show that in equilibrium (i. e. the stationary state of the dynamics) this approach produces the canonical ensemble at temperature T (k_B denotes the Boltzmann constant).
Hints:

- Consider the extended phase–space density $\rho_{ext}\left(\{\vec{r}_i\},\{\vec{p}_i\},\zeta\right)$, as well as

$$\rho\left(\{\vec{r}_i\},\{\vec{p}_i\}\right)=\int_{-\infty}^{+\infty}d\zeta\,\rho_{ext}\left(\{\vec{r}_i\},\{\vec{p}_i\},\zeta\right). \tag{9}$$

- Construct the proper Liouville operator for the dynamics of ρ_{ext} by reading off the Kramers–Moyal coefficients.
- Search for the stationary solution of the equation, and show that you can solve this problem by the product ansatz

$$\rho_{ext}=\exp\left(-\beta\mathcal{H}\right)\Psi\left(\zeta\right), \tag{10}$$

where $\beta=1/(k_BT)$, and $\mathcal{H}$ denotes the Hamiltonian of the original N–particle system (without coupling to the thermostat ζ). What function do you obtain for $\Psi(\zeta)$?

4. **Stiff Polymer Chains and Transfer Matrices**
We consider a simple model for a polymer chain in terms of a random walk on a three–dimensional simple–cubic lattice. For simplicity, we assume a unit system in which the lattice spacing is unity. More precisely, we model the chain as a sequence of bond vectors $\vec{l}_i$, $i=1,2,\ldots,N$, where each of the $\vec{l}_i$ can only be one of the six vectors $(\pm1,0,0)$, $(0,\pm1,0)$, $(0,0,\pm1)$. Stiffness is modeled by an energy parameter $\epsilon>0$, such that the Hamiltonian is

$$\mathcal{H}=-\epsilon\sum_{i=1}^{N}\delta(\vec{l}_i,\vec{l}_{i+1}), \tag{11}$$

where $\delta(\vec{l}_i,\vec{l}_{i+1})$ is one if $\vec{l}_i=\vec{l}_{i+1}$, and zero otherwise. In other words, the stretched conformation (in which the consecutive bonds $\vec{l}_i$ and $\vec{l}_{i+1}$ are aligned) is favored by the energy $-\epsilon$, while all other bond angles have energy zero. For simplicity, we assume periodic boundary conditions ($\vec{l}_{N+1}=\vec{l}_1$), i. e. we introduce an "artificial" energy between the first and the last bond — this contribution does ultimately not matter in the limit of long chains, $N\to\infty$. We assume a constant–temperature ensemble. Calculate the chain's specific heat as a function of temperature, in the limit of large N, by making use of the transfer matrix technique.

5. **Interface Profile**
Consider a one–dimensional field theory. The field is the magnetization profile $m(x)$ (m is a simple scalar quantity). The free energy for this profile is given by the functional

$$\mathcal{F}[m(x)]=\int_{-\infty}^{\infty}dx\,\left[\frac{R}{2}\left(\frac{dm}{dx}\right)^2-\frac{r}{2}m^2+\frac{u}{4!}m^4\right]. \tag{12}$$

Here $R>0$, $r>0$, $u>0$ are some parameters of the model. If we assume that $m(x)$ is homogeneous (constant), then we have a free energy per unit length, as a function of magnetization,

$$f(m)=-\frac{r}{2}m^2+\frac{u}{4!}m^4. \tag{13}$$

(a) Plot $f(m)$. Show that the minimization with respect to m yields two possible values $m = \pm m_{sp} =?$ (spontaneous magnetization). For this reason, the theory is a (Mean Field) model for phase coexistence.

(b) Now consider the full functional. Minimize $\mathcal{F}$ with respect to the profile. Show that this is analogous to classical mechanics. Make use of the analogue of the energy conservation theorem in classical mechanics. Calculate the profile for the boundary conditions $m \to -m_{sp}$ for $x \to -\infty$, and $m \to +m_{sp}$ for $x \to +\infty$. You may assume that the coordinate system is chosen such that $m(x = 0) = 0$.

Hints:

- The gradient–square term in $\mathcal{F}$ models the interfacial tension, i. e. the tendency of the system to build up domains of homogeneous magnetization. The term "punishes" every configuration that is inhomogeneous.
- It is useful to introduce the reduced variable $\mu = m/m_{sp}$, as well as a suitably non–dimensionalized spatial coordinate.
- The value of the "energy" can be deduced from the boundary conditions.
- $$\int \frac{dx}{1-x^2} = \frac{1}{2} \ln \frac{1+x}{1-x}. \tag{14}$$

6. **Lattice Boltzmann Equilibrium Populations**
We consider a lattice Boltzmann method on a cubic lattice with populations $n_i(\vec{r}, t)$ and discrete velocities $\vec{c}_i$. For simplicity, we assume a unit system where both the lattice spacing and the time step are unity. The conserved mass density ρ, the conserved momentum density $\vec{j}$, and the flow velocity $\vec{u}$ are then given by

$$\rho = \sum_i n_i, \tag{15}$$

$$\vec{j} = \sum_i n_i \vec{c}_i, \tag{16}$$

$$\vec{u} = \rho^{-1} \vec{j}. \tag{17}$$

For the equilibrium populations, we start from the ansatz

$$n_i^{eq}(\rho, \vec{u}) = w_i \rho \left(1 + A \vec{u} \cdot \vec{c}_i + B(\vec{u} \cdot \vec{c}_i)^2 + C u^2\right), \tag{18}$$

and make use of the fact that the weights w_i must be the same within each velocity shell, such that they obey the moment relations

$$\sum_i w_i = 1, \tag{19}$$

$$\sum_i w_i c_{i\alpha} = 0, \tag{20}$$

$$\sum_i w_i c_{i\alpha} c_{i\beta} = \sigma_2 \, \delta_{\alpha\beta}, \tag{21}$$

$$\sum_i w_i c_{i\alpha} c_{i\beta} c_{i\gamma} = 0, \tag{22}$$

$$\sum_i w_i c_{i\alpha} c_{i\beta} c_{i\gamma} c_{i\delta} = \kappa_4 \, \delta_{\alpha\beta\gamma\delta} + \sigma_4 \left(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}\right). \tag{23}$$

Here the greek indices denote Cartesian directions, $\delta_{\alpha\beta}$ is the standard Kronecker delta, and $\delta_{\alpha\beta\gamma\delta}$ is unity if all four indices coincide, while it is zero otherwise. σ_2, κ_4, and σ_4 are

parameters that depend on the specific choice of the weights w_i. It can then be shown (*not* your task!) that on *any* cubic lattice the relations

$$\kappa_4 = 0, \tag{24}$$
$$\sigma_4 = \sigma_2^2 \tag{25}$$

should hold — otherwise the zeroth, first, and second velocity moments of n_i^{eq} would have incorrect values. With correctly chosen w_i one then finds $c_s^2 = \sigma_2$ for the speed of sound and

$$n_i^{eq}(\rho, \vec{u}) = w_i \rho \left(1 + \frac{\vec{u} \cdot \vec{c}_i}{c_s^2} + \frac{(\vec{u} \cdot \vec{c}_i)^2}{2c_s^4} - \frac{u^2}{2c_s^2}\right), \tag{26}$$

which is true on any cubic lattice (also *not* your task!). Equations 19, 24, and 25 then form a set of conditions for the weights. One possible solution is the D3Q19 model discussed in the lecture. Your task is now to consider the D2Q9 model in two dimensions, where we have a simple square lattice (i. e. a 2D cubic lattice), and the nine velocity vectors

- $\vec{c}_0 = (0, 0)$, corresponding to a weight w_0;
- $\vec{c}_1 = (1, 0)$, $\vec{c}_2 = (0, 1)$, $\vec{c}_3 = (-1, 0)$, $\vec{c}_4 = (0, -1)$, corresponding to the weight $w_1 = w_2 = w_3 = w_4 = w_I$ for neighbor shell I;
- $\vec{c}_5 = (1, 1)$, $\vec{c}_6 = (-1, 1)$, $\vec{c}_7 = (-1, -1)$, $\vec{c}_8 = (1, -1)$, corresponding to the weight $w_5 = w_6 = w_7 = w_8 = w_{II}$ for neighbor shell II.

Find the weights w_0, w_I, w_{II} for this lattice Boltzmann algorithm, and give the value for c_s^2 in natural simulation units.

Hint: Consider certain Cartesian directions and find the values of σ_2, σ_4, and κ_4 in terms of w_0, w_I, w_{II}. Then solve the system of equations 19, 24, and 25.