

## PROBLEMS FOR MONTE CARLO

### 1. noughts and crosses (tic tac toe) in periodic boundary conditions

			X					
		X	O	O				
					X			

You may remember the game of noughts and crosses (or tic tac toe). The two players sequentially put down an X or an O respectively. To win you need 3 in a row. This game should always lead to a tie (if you don't make an error). To spice it up a bit, try to play in periodic boundary conditions. An example configuration is given above. Continue this into p.b.c. Who has won? Convince yourself that whoever starts can always win.

Can you think of alternate rules for the game in p.b.c.? For example, you could play to see who has the maximum length in a row, or who has the highest percentage of pieces in a row.

### 2. Importance sampling

Suppose you want to calculate the integral  $\int_0^1 (1+x^2)dx$  by a MC simulation.

a) What would the standard deviation be if you did a straightforward calculation with  $M$  points?

b) What would the standard deviation be if you used  $1+x$  as your importance sampling function?

### 3. – fluctuations

David Kofke has written a very nice Java applet to illustrate fluctuations

(<http://www.cheme.buffalo.edu/kofke/applets/Fluctuations.html>)

Download this applet, and measure the fluctuations in the local density as a function of “volume”. The applet is fairly simple, i.e. you need to make up a measure for the volume, and estimate the fluctuations.

Plot the fluctuations v.s. the number of particles  $N$  in the box. How Do they scale as you expect them to?

#### 4. Reminder of classical statistical mechanics

In the course we extensively use the canonical partition function of a classical fluid. For that reason it is useful for you to gain some familiarity with manipulating these partition functions and the free-energies that ensue. Consider a system interacting with a (pair) potential  $V(\mathbf{r})$ . Its canonical partition function has the form:

$$Q(N, V, T) = \frac{1}{\Lambda^{3N} N!} Z(N, V, T) \quad (6.29)$$

where the de Broglie thermal wavelength is given by  $\Lambda = (2\pi m k_B T)^{\frac{1}{2}}$  and the configurational integral can be written as:

$$Z(N, V, T) = \int_V d\mathbf{r}^N \exp[-\beta \mathcal{V}(\mathbf{r}^N)] \quad (6.30)$$

(a) Show that for an ideal gas  $Z(N, V, T) = V^N$

(b) Show that the free-energy per particle is given by

$$\frac{\beta A^{id}}{N} = \log[\rho \Lambda^3] - 1 \quad (6.31)$$

(c) From this, derive the pressure  $\beta P(\rho)$

(d) Derive the chemical potential  $\mu = \left(\frac{\partial A}{\partial N}\right)_{V,T}$

(e) The grand-canonical partition function can be rewritten as

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} \exp[N\beta\mu] Q(N, V, T) \quad (6.32)$$

derive the form of the grand-canonical partition function for an ideal gas. Derive from this the pressure of an ideal gas in terms of  $\mu$ . Does this agree with the results for  $\mu$  and  $P(\rho)$  you found for the canonical ensemble?

(f) Do the same for the isobaric ensemble, where your variables are  $N, P, T$ .

(g) For low density gasses, the pressure can be approximated with a second virial coefficient:

$$\beta P = \rho + B_2 \rho^2 \quad (6.33)$$

For such a system, what is the excess free-energy defined by

$$A = A^{id} + A^{ex} \quad (6.34)$$

What is the chemical potential  $\mu$ ?

What is the form of the grand-canonical partition function  $\Xi(\mu, V, T)$ ?

### 5. Errors in data (optional)

Go to <http://www-theor.ch.cam.ac.uk/people/ardlouis/teaching/random.dat> and download the file. These are 25,000 random data points from a simulation. Using a program like Excell, try to estimate the true standard deviation in this data. I.e. use the block averaging method of chapter 1. Do you need to throw away any initial points?

### 6. Heat capacity (from Frenkel and Smit 2002)

In the NVT ensemble, the heat capacity is given by

$$\langle (E - \langle E \rangle)^2 \rangle_{NVT} = k_B T^2 C_V. \quad (6.35)$$

**a)** In a typical simulation, one doesn't calculate the fluctuations in the total energy, but only in the potential energy. Is it then still possible to calculate the heat capacity? Explain.

**b)** The heat capacity can also be calculated by differentiating the total energy of a system with respect to temperature. Discuss the advantages or disadvantages of this approach.

### 7. Scaling as a MC move (from Frenkel and Smit 2002)

Consider as system in which the energy is a function of one variable ( $x$ ) only,

$$\exp[-\beta U(x)] = \theta(x)\theta(1-x) \quad (6.36)$$

in which  $\theta(x)$  is the Heaviside function  $\theta(x < 0) = 0$  and  $\theta(x > 0) = 1$ . We wish to calculate the distribution of  $x$  in the canonical ensemble. We will consider two possible algorithms (we will use  $\delta > 0$ ):

**i)** Generate a random change in  $x$  between  $[-\delta, \delta]$ . Accept or reject the new  $x$  according to its energy.

**ii)** Generate a random number  $\phi$  between  $[1, 1 + \delta]$ . With a probability of 0.5, invert the value of  $\phi$  thus obtained. The new value of  $x$  is obtained by multiplying  $x$  with  $\phi$ .

**a.** Derive the correct acceptance/rejection rules for both schemes

**b.** What happens when acceptance rule of method (i) is used in the algorithm of method (ii)?

### 8. Multicomponent Simulation (from Frenkel & Smit 2002)

We consider developing a grand-canonical MC scheme for a mixture of two components. Assume the temperature is  $T$  and the chemical potentials of the two components are  $\mu_1$  and  $\mu_2$ .

a) To add or remove particles the following scheme is used

- Select at random to add or remove a particle
- Select at random a component
- Add or remove a particle of this component

Derive the acceptance rules for these trial moves.

b) An alternative set of trial moves would be:

- Select at random to add or remove a particle
- Select at random a particle, independent of its identity.

Does this scheme obey detailed balance if the previous acceptance rules are used? If not, how might this be corrected?

### **Widom insertion**

You may wonder why we only discussed particle addition moves in the section on Widom insertion. To see why, derive the expression, similar to Eq.2.19, that you would have to average over if you tried random particle deletion moves (again only testing for the deletion w/o actually performing the move). Why would this not work very well (think e.g. of applying it to Hard Sphere)?

## PROBLEMS FOR MOLECULAR DYNAMICS

9. The total linear momentum of a system of  $N$  particles is defined as  $\mathbf{P} = \sum_i^N \mathbf{p}_i$  where  $\mathbf{p}_i$  is the momentum of particle  $i$ . Show that  $\mathbf{P}$  is a constants of motion for a potential of the form of Eq. 4.5.
10. A modification of the Verlet algorithm predating velocity Verlet which also makes explicit use of velocity as iteration variable is the leap-frog algorithm. In this scheme the position and velocity are half a time step out of step. The velocities at half integer time are defined as

$$\mathbf{v}_i(t - \delta t/2) = \frac{\mathbf{r}_i(t) - \mathbf{r}_i(t - \delta t)}{\delta t}$$

$$\mathbf{v}_i(t + \delta t/2) = \frac{\mathbf{r}_i(t + \delta t) - \mathbf{r}_i(t)}{\delta t}$$

Based on these definitions the following sequence of update steps is used to propagate position and velocity, one “leaping” over the other with a full time step.

$$\mathbf{v}_i(t + \delta t/2) = \mathbf{v}_i(t - \delta t/2) + \frac{\delta t}{m_i} \mathbf{f}_i(t)$$

$$\mathbf{r}_i(t + \delta t) = \mathbf{r}_i(t) + \delta t \mathbf{v}_i(t + \delta t/2)$$

Velocity at time  $t$  for the evaluation of total energy is obtained as

$$\mathbf{v}_i(t) = \frac{1}{2} (\mathbf{v}_i(t + \delta t/2) + \mathbf{v}_i(t - \delta t/2))$$

Show that the leap-frog algorithm is equivalent to the Verlet algorithm.

11. Sketch in the schematic fashion of Fig. 5.3 the radial distribution function of a low temperature body centered (bcc) solid, indicating the position and coordination numbers of the first two peaks assuming a repulsive diameter of  $\sigma$ . Bcc structures are not uncommon for metals. Describe how the RDF will change when a bcc metal melts. Will the area under the first peak increase or decrease? Explain why.
12. The pair correlations in binary mixtures  $AB$  are described by three radial distribution functions, two for like-like correlations,  $g_{AA}(r)$  and  $g_{BB}(r)$ , and one for correlations between particles of different species,  $g_{AB}(r)$ . Figure P1 shows an example of a RDF between like particles and unlike particles for a molten salt.
- a Which of the two curves represents the mixed RDF  $g_{AB}$ ? Explain your reasoning.
  - b Assume the like-like RDF in the figure is  $g_{AA}$  and that the ionic radii for  $A$  and  $B$  are the same, describe how  $g_{BB}$  will differ from  $g_{AA}$ .
  - c The ionic radius of the cations is usually (but not always) smaller than the radius for the anion. For NaCl the ratio is  $r_{Cl^-} \approx 1.5r_{Na^+}$ . Make a sketch of the three RDF's for molten NaCl indicating where you expect the first peaks and give also an estimate of the coordination numbers.

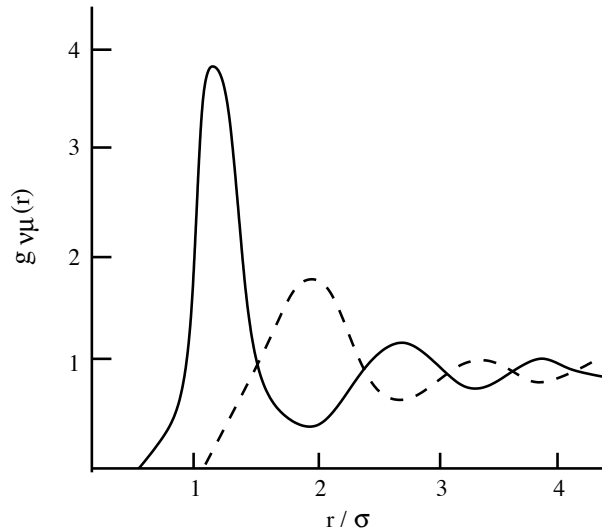


Fig. P1: RDF's for a liquid binary mixture (molten salt, see question 8)

13. Hydrogen atoms are strongly bonded in most weak acids HA giving sharp peaks in the H-A radial distribution function at  $r \approx 1\text{\AA}$  which are well separated from the intermolecular structure at distances  $r > 1.5\text{\AA}$  due to hydrogen bonding to the aqueous solvent. The half width of the intra-molecular HA peak is typically  $\approx 0.1\text{\AA}$ . Under these conditions we can model H-A the intra-molecular peak in the RDF by a Gaussian

$$g_{\text{intra}}(r) = g_0 \exp \left[ -\frac{(r-d)^2}{2\Delta} \right]$$

with  $d = 1\text{\AA}$  and  $\Delta = 0.1\text{\AA}$  (see figure P2). Assuming that at a concentration of 0.1M none of the HA molecules is dissociated, estimate the maximum value of the intra molecular RDF, i.e compute  $g_0$ . (*Hint:* Use the fact that you know the coordination number at the coordination radius  $R_c$  (see figure) between the intra and intermolecular part of the RDF).

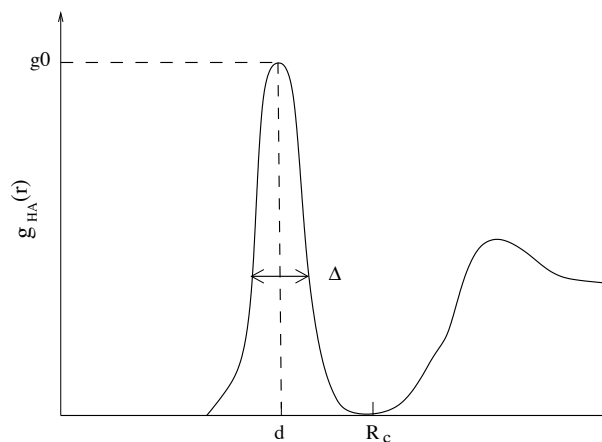


Fig. P2: Hydrogen (H) conjugate base (A) RDF for a weak acid

14. Show that the contribution to the virial pressure of the repulsive term in the 12-6 Lennard-Jones interaction is positive and the contribution of the attractive term is negative.
15. Liquid nitrogen can be modeled by a system dimers with harmonic interaction between atoms in the same molecule and a 12-6 Lennard Jones pair potential  $v(r)$  for the interaction between atoms in different molecules:

$$U = \sum_{i=1}^N \frac{k_d}{2} (|\mathbf{r}_{i,1} - \mathbf{r}_{i,2}| - d_0)^2 + \sum_{i < j}^N \sum_{\alpha, \beta=1}^2 v(|\mathbf{r}_{i,\alpha} - \mathbf{r}_{j,\beta}|)$$

where  $\mathbf{r}_{i\alpha}$  is the position vector of atom  $\alpha = 1, 2$  in molecule  $i = 1 \dots N$ .  $d_0$  is the equilibrium bond length. In a low density gas the effect of intermolecular interactions (collisions) on the vibrations can be neglected. Show that under those conditions the intra molecular contribution to the virial pressure of the NN stretch is independent of the spring constant.

16. Using the definition of a time correlation function in terms of a time average over reference times (Eq. 5.29), show that the auto time correlation function of the function  $A(t) = \cos \omega t$  averaged over a duration  $\Delta t \gg 2\pi/\omega$  is given by

$$C_{AA}(\tau) = \frac{1}{2} \cos \omega \tau$$

Similarly find the time correlation for a superposition of two harmonic motions

$$A(t) = a_1 \cos(\omega_1 t) + a_2 \cos(\omega_2 t)$$

17. The velocity autocorrelation can tell us something about the time step  $\delta t$  used in the numerical integration of the equations of motion. Assuming that this was the Verlet algorithm, what is the maximum value of the time step  $\delta t$  that could have been used to produce the velocity autocorrelation function shown in the figure? Briefly indicate your reasons for choosing this value.
18. Make a qualitative sketch of the velocity autocorrelation functions of CO molecules in the solid. Make also a sketch of the corresponding spectrum (Fourier transform) and make an assignment of the bands (peaks).
19. Apply the exponential approximation of Eq. 5.47 to the velocity autocorrelation function, and determine the mean squared displacement (Eq. 5.64) as a function of time. Make a plot of what you have found. The velocity auto correlation of Fig. P3 is, however, clearly not of exponential form. Sketch in your figure the changes as a result of the oscillation in Fig. P3. How can this effect be interpreted?

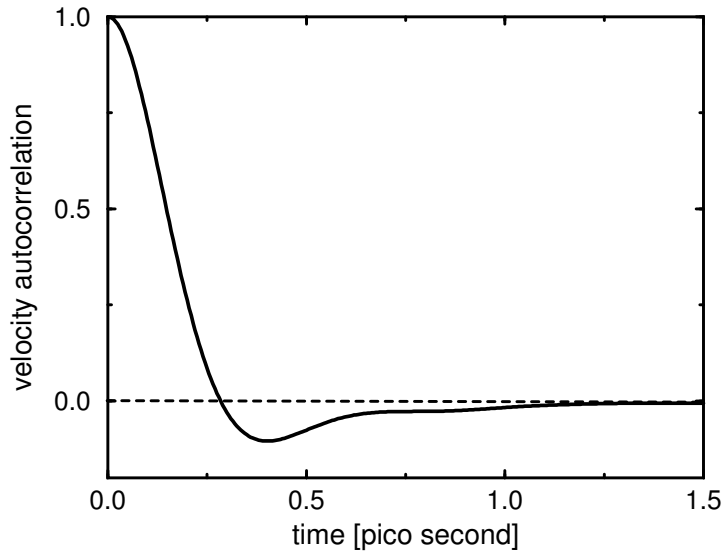


Fig. P3: Velocity auto correlation function for a monatomic liquid.

20. From experimental observation we know that  $D = 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$  is a typical value for the self diffusion constant in simple liquids. Using the exponential approximation to the velocity autocorrelation function

$$\langle \mathbf{v}(\tau) \cdot \mathbf{v}(0) \rangle \approx \langle v^2 \rangle e^{-t/\tau}$$

give an estimate for the correlation time  $\tau$  for liquid argon at the temperature of  $T = 85\text{K}$ .

21. The orientational degrees of freedom of a diatomic molecule AB can be described by the coordinate vector  $\mathbf{d} = \mathbf{r}_A - \mathbf{r}_B$ , connecting the atoms. Explain why in the gas phase the thermal average of the cartesian coordinates of  $\mathbf{d}$  vanishes. Since this is the case, we can define the orientational time correlation function as

$$c_{dd}(\tau) = \langle \mathbf{d}^2 \rangle^{-1} \langle \mathbf{d}(\tau) \cdot \mathbf{d}(0) \rangle$$

where  $\sqrt{\langle \mathbf{d}^2 \rangle} = d_0$  with  $d_0$  the equilibrium bond length (neglecting the effect of vibrations). At low density  $c_{dd}$  exhibits a time dependence similar to the velocity autocorrelation function of Fig.P3 with (at least) one oscillation. For the nitrogen dimer  $N_2$  at ambient temperature ( $T=298\text{K}$ ) the first minimum is at  $\tau = 0.41 \text{ ps}$ . Use this value to estimate the bond length  $d_0$  (*Hint*: use the classical approximation for rotational kinetic energy).

22. Show that the total linear momentum of a system of  $N$  particles coupled to a Nosé thermostat is no longer a constant of motion. How will the total momentum change during periods of sustained heating? Will it increase or decrease?
23. Nosé thermostats coupled to weakly interacting systems, such as the normal modes of a molecule, can develop oscillatory behavior comparable to a stationary non-equilibrium state. This can be sometimes be avoided by introducing a second thermostat controlling

the temperature of the first. The equation of motion of such a two thermostat system is

$$\begin{aligned}\ddot{\mathbf{r}}_i &= \frac{\mathbf{f}_i}{m_i} - \zeta_1 \dot{\mathbf{r}}_i \\ \dot{\zeta}_1 &= \frac{1}{Q_1} \left[ \sum_{i=1}^N m_i \dot{\mathbf{r}}_i^2 - 3Nk_B T \right] - \zeta_1 \zeta_2 \\ \dot{\zeta}_2 &= \frac{1}{Q_2} [Q_1 \zeta_1^2 - k_B T]\end{aligned}$$

Find the total energy function which is conserved by this set of equations of motion and show that it is in fact a constant of motion.

24. Instead of using the quadratic bond constraint of Eq. 6.15 we can also keep the bond length between particles 1 and 2 fixed by imposing the distance constraint  $r_{12} - d_0 = 0$ . Derive an expression for the exact (velocity dependent) Lagrange multiplier for this constraint (similar to Eq. 6.22). What are the forces of constraint acting on atom 1 and 2?