

Exercises

10.2 Pair distributions and molecular dynamics.^{1,2} (Computation) ③

Many scattering experiments measure the correlations between atomic positions. Let our system have N particles in a volume V .³ The mean density in a system with atoms at positions \mathbf{x}_i

$$\rho(\mathbf{x}) = \left\langle \sum_i \delta(\mathbf{x} - \mathbf{x}_i) \right\rangle, \quad (10.80)$$

and the density–density correlation function⁴

$$C(\mathbf{x}, \mathbf{x}') = \left\langle \sum_{i, j \neq i} \delta(\mathbf{x} - \mathbf{x}_i) \delta(\mathbf{x}' - \mathbf{x}_j) \right\rangle \quad (1)$$

are used to define the *pair correlation function* $g(\mathbf{x}, \mathbf{x}')$:

$$g(\mathbf{x}, \mathbf{x}') = \frac{C(\mathbf{x}, \mathbf{x}')}{\rho(\mathbf{x})\rho(\mathbf{x}')} = \frac{C(\mathbf{x} - \mathbf{x}')}{(N/V)^2}. \quad (10.82)$$

Here the last equality is valid for homogeneous systems like liquids and gases.⁵

(a) Show analytically from equation 10.80 that $\rho(\mathbf{x})$ for a homogeneous system is the indeed the average density N/V . Show that $g(\mathbf{x}, \mathbf{x}') = g(\mathbf{x} - \mathbf{x}') = g(\mathbf{r})$, where

$$g(\mathbf{r}) = \left\langle \frac{V}{N^2} \sum_{i, j \neq i} \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle \quad (2)$$

and $\mathbf{r}_{ij} = \mathbf{x}_i - \mathbf{x}_j$ is the vector separating the positions of atoms i and j . If the system is homogeneous and the atoms are uncorrelated (i.e., an ideal gas), show that $g(\mathbf{r}) \equiv 1$. If the potential

energy is the sum of pair interactions with potential $E(\mathbf{r}_{ij})$, write the potential energy as an integral over three-dimensional space \mathbf{r} involving N , V , $g(\mathbf{r})$, and $E(\mathbf{r})$.

Usually $g(\mathbf{r}) \rightarrow 1$ as $r \rightarrow \infty$; the correlations die away as the separation grows.

Liquids and gases are also isotropic; the pair correlation function g must be rotation invariant, and hence can only depend on the distance $r = |\mathbf{r}|$. A typical molecular dynamics code will have a fast `NeighborLocator` routine, which will return the `HalfNeighbor` pairs of atoms $j < i$ with $|r_{ij}|$ less than a given cut-off. A histogram of the distances between these nearby points, suitably rescaled, is a convenient way of numerically estimating the pair correlation function. Let the histogram $h(r_n)$ give the number of such pairs in our system with $r_n < r < r_n + \Delta r$.

(b) For an isotropic, homogeneous system in three dimensions, show

$$g(\mathbf{r}) = \frac{2V}{N^2} \frac{h(r)}{4\pi r^2 \Delta r}. \quad (10.84)$$

What is the corresponding formula in two dimensions?

Download our molecular dynamics software [10] from the text web site [129]. In our simulation, we use the Lennard–Jones potential, in which all pairs of atoms interact with an energy with a short-range repulsion $\sim 1/r^{12}$ and a long-range (van der Waals) attraction $\sim 1/r^6$:

$$E_{\text{pair}}(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right). \quad (10.85)$$

¹From *Statistical Mechanics: Entropy, Order Parameters, and Complexity* by James P. Sethna, copyright Oxford University Press, 2007, page 233. A pdf of the text is available at pages.physics.cornell.edu/sethna/StatMech/ (select the picture of the text). Hyperlinks from this exercise into the text will work if the latter PDF is downloaded into the same directory/folder as this PDF.

²This exercise was developed in collaboration with Neil W. Ashcroft and Christopher R. Myers.

³We will use periodic boundary conditions, so the edges of the container do not break the translational symmetry.

⁴Warning: In the theory of liquids, C is used for another function, the Ornstein–Zernike direct correlation function.

⁵The pair correlation function represents the degree to which atomic positions fluctuate together, beyond the clumping implied by the possibly inhomogeneous average density. For example, three-dimensional crystals have a long-range broken translational symmetry; $\rho(\mathbf{x})$ will have peaks at the lattice sites even after averaging over thermal vibrations.

Lennard–Jones is a reasonable approximation for the interatomic forces between noble gas atoms like argon. In our simulation, we choose the length scale σ and the energy scale ϵ both equal to one.

(c) Plot the Lennard–Jones pair potential as a function of r , choosing a vertical scale so that the attractive well is visible. Where is the minimum-energy spacing between two atoms? Can you see why the repulsion is called ‘hard core’?

Gas. We start with a simulated gas, fairly near the vapor pressure.

(d) Simulate a two-dimensional gas of Lennard–Jones atoms, at a temperature $T = 0.5\epsilon$ and a density $\rho = 0.05/\sigma^2$. Calculate the pair distribution function for the gas for $0 < r < 4\sigma$. Note the absence of pairs at close distances. Can you observe the effects of the attractive well in the potential, both visually and in the pair correlation function?

In a low-density, high-temperature gas the correlations between atoms primarily involve only two atoms at once. The interaction energy of a pair of atoms in our system is $E_{\text{pair}}(r)$, so in this limit

$$g_{\text{theory}}(r) \propto \exp(-E(r)/k_B T). \quad (3)$$

Since $E(r) \rightarrow 0$ and $g(r) \rightarrow 1$ as $r \rightarrow \infty$, the constant of proportionality should be one.

(e) Compare $g(r)$ from part (d) with g_{theory} for a system with density $\rho = 0.05/\sigma^2$. Do they agree well? Do they agree even better at higher temperatures or lower densities, where multi-particle interactions are less important?

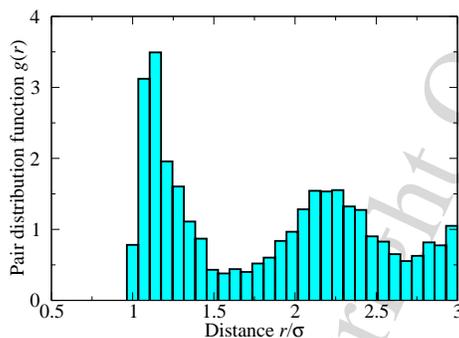


Fig. 10.15 Pair distribution function $g(r)$ for a two-dimensional Lennard–Jones liquid.

Liquid. We now turn to a liquid, at the same temperature as our gas but at a higher density.

(f) Simulate a liquid, at $\rho = 0.75/\sigma^2$ and $T = 0.5$. Note from the animation that each atom in the two-dimensional simulation has around six nearest-neighbors, at nearly the minimum-energy distance. Calculate the pair distribution function. Can you explain the features you see in terms of nearest-neighbors and second-nearest neighbors?

(g) If we define the coordination number of a liquid atom as all those with distances less than the position of the dip between nearest and next-nearest neighbors in $g(r)$, what is the mean number of near neighbors for your two-dimensional liquid?

In most (three-dimensional) simple elemental liquids, the coordination number defined by this criterion is between 11 and 11.5. (The close-packed crystals have twelve nearest neighbors). The main exceptions are the group IV elements (carbon, silicon, germanium, ...) where the bonding is strongly angle dependent and the number of liquid near neighbors is smaller, around 5.5; their crystalline phases have three or four covalently-bonded neighbors.

Crystal. In a three-dimensional crystal, the atoms vibrate around their equilibrium lattice positions (with only rare hops between lattice sites as atoms exchange with one another or vacancies move through the crystal). If these vibrations become large compared to the lattice constant, then surely the crystal will melt. The *Lindemann criterion* notes that for simple crystals, melting usually occurs when the thermal vibrations away from the lattice positions are about 10% of the interatomic spacing.

(Note how weird this is. A three-dimensional crystal, billions of atoms across, thermally vibrating almost enough to melt, still holds its atoms in rigid registry within fractions of an Angstrom.)

This is not true in two dimensions, where the lattice is not as stiff and thermal fluctuations are more severe.⁶ The Lindemann criterion of course also implies that the typical variation in the nearest-neighbor separations for three-dimensional crystals stays much smaller than the lattice constant at the

⁶The theory of two-dimensional crystals and how they melt has spawned many beautiful theoretical and experimental studies; look for works on the *Kosterlitz–Thouless–Halperin–Nelson–Young* transition.

melting point. Is this version of the Lindemann criterion true of two-dimensional crystals?

(h) *Simulate a crystal, at $T = 0.1$ starting from a hexagonal crystal with interatomic spacing approximating the minimum of the pair potential. Calculate the isotropic spatial average of the pair correlation function.*⁷ *By what percentage does the nearest-neighbor separation fluctuate? Are they small compared to the lattice constant? Also, can you identify which neighbors on the hexagonal lattice correspond to the second-nearest-neighbor and the third-nearest-neighbor peaks in $g(r)$?*

⁷That is, use the routines you've developed for liquids and gases, ignoring the spatially dependent $\rho(x)$ in equation 10.82 and discussed in note 5. This average still gives the correct potential energy.