Tutorial: BD Exercises Solution

February 06, 2026

Note: Students are requested to be awarded marks leniently where numerical values are approximate. The questions have been designed to be sufficiently challenging to assess the depth of understanding and justify the overall evaluation.

Maximum marks: 70

Answers

1. **Verification of the Einstein Diffusion Equation**

   The Einstein diffusion relation for Brownian motion is

   $$D = \frac{k_\mathrm{B}T}{\gamma},$$

   which predicts a linear dependence of the diffusion coefficient D on temperature T, inverse friction γ^{-1}, and inverse mass m^{-1}.

   - **Step 1: Dependence on friction coefficient**
     The diffusion coefficient was computed for $\gamma^{-1} = 0.1, 0.3, 0.6, 1.0$, while keeping the mass $m = 1$ and $k_\mathrm{B}T = 1.0$ fixed.
     The resulted data for the γ^{-1} vs D is pasted below.

     ```
     0.1  0.0998
     0.3  0.2993
     0.6  0.5982
     1.0  0.9954
     ```

     [2.5 marks]

   - **Step 2: Dependence on temperature**
     Simulations were performed at temperatures $k_\mathrm{B}T = 1, 2, 3, 7$, with fixed $\gamma^{-1} = 0.1$ and $m = 1$. The plot shown in Figure 2 (`t_vs_d.png`) demonstrates a linear increase of the diffusion coefficient with temperature.
     The resulted data for the k_BT vs D is pasted below.

     ```
     1.0    0.0998
     2.0    0.1996
     3.0    0.2993
     7.0    0.6985
     ```

     [2.5 marks]

- **Step 3: Dependence on mass**

  The diffusion coefficient was evaluated for particle masses $m = 1, 2, 3, 6$, while keeping $k_{\mathrm{B}}T = 1.0$ and $\gamma^{-1} = 0.1$ fixed.

  The resulted data for the $k_B T$ vs D is pasted below.

  ```
  1.0   0.0998
  2.0   0.0499
  3.0   0.0333
  6.0   0.0166
  ```

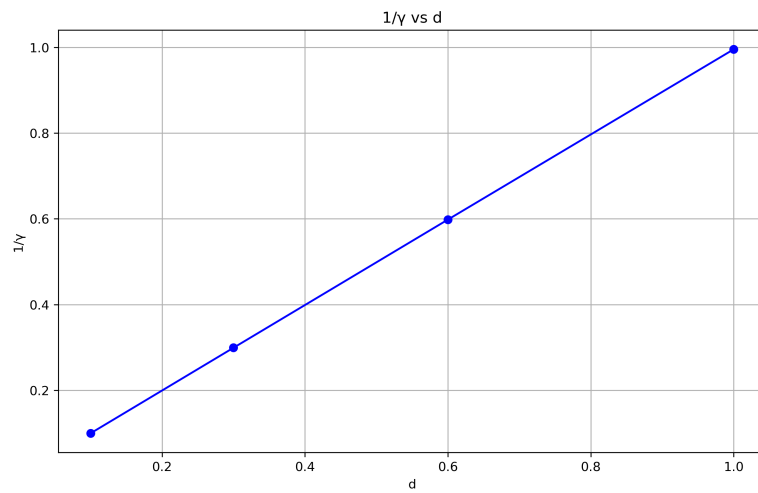 **[2.5 marks]**

- **Step 4: Discussion**

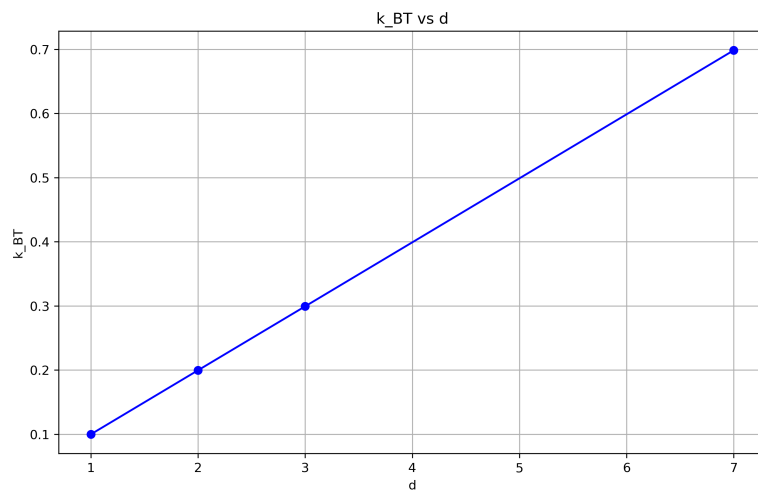Figure 1: Diffusivity is plotted as a function of γ^{-1}.

Figure 2: Diffusivity has been shown as the function of temperature.
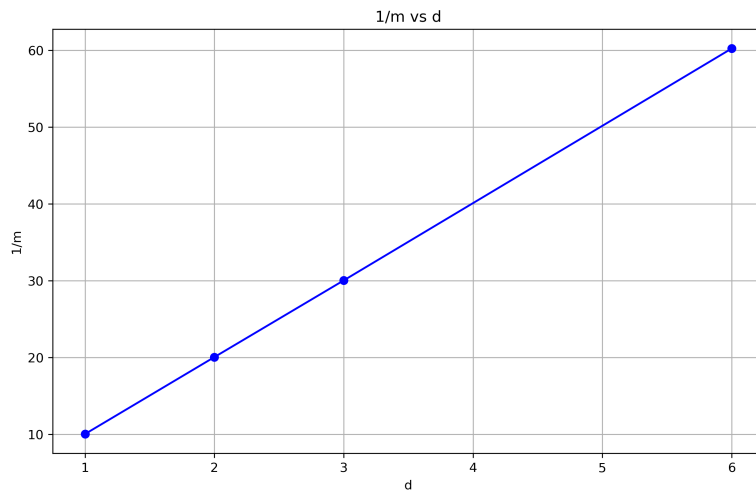
Figure 3: Diffusivity is plotted as a function of mass m.

From Figures 1-3, the following relations are observed:

$$D \propto \gamma^{-1}, \qquad D \propto k_{\mathrm{B}}T, \qquad D \propto m^{-1}.$$

All three dependencies are approximately linear within numerical uncertainty, thereby validating the Einstein diffusion equation for the simulated system.

[2.5 marks]

2. **Dumbbell-Shaped Patchy Particle System**

- **Step 1: Constructing a dumbbell-shaped molecular template**
  The dumbbell-shaped molecule consists of three atoms: - One central hard-core atom (core) - Two patch atoms located on opposite ends of the core
  The complete `.mol` file is provided below:

```
# Dumbbell-shaped molecule template

3 atoms           # Total number of atoms in the molecule

# ---------------- COORDINATES ----------------
# Format: atom_index   x   y   z (in reduced LJ units)
Coords
1  1.0  1.0  1.0    # Core atom at the center
2  1.0  1.0  1.5    # Patch atom on +z direction (bond length 0.5)
3  1.0  1.0  0.5    # Patch atom on -z direction (bond length 0.5)

# ---------------- ATOM TYPES ----------------
# Format: atom_index   type
Types
1   1    # Core atom
2   2    # Patch atom
3   2    # Patch atom
```

Justification: - The molecule is symmetric along the z-axis to form a dumbbell shape. - The central core atom (type 1) is bonded to both patch atoms (type 2) with fixed bond length 0.5 LJ units.

Note: Students are supposed to check just the distance of the patches from the core, such that patches are supposed to be inline with the core and with each other forming dumbbell shaped, while origin of the dumbbell can be placed anywhere, e.g., at $0.0, 0.0, 0.0$.

[5.0 marks]

- **Step 2: Phase behavior**
  Simulations were performed over a range of temperatures. At lower temperatures ($k_\mathrm{B}T < 0.15$), the system exhibits liquid-like chain-forming behavior, as shown in Figure 4.
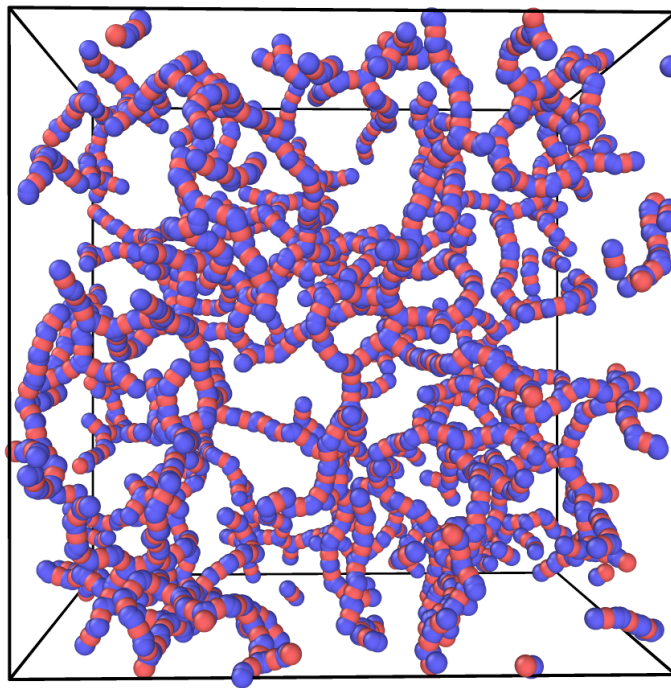

Figure 4: Liquid state defined by the chain like structure.

Core and patch particles are clearly distinguishable by color and size. The corresponding temperature at which stable chains are observed is reported.

[5.0 marks]

- **Step 3: Stability discussion**
  The chain structures are metastable and persist over long simulation times at lower temperatures.

At low temperatures, thermal motion is insufficient to break directional patch bonds, leading to metastable chains.

At higher temperatures, thermal fluctuations dominate, resulting in chain breakup which leads system to the lowest potential energy state, which has more than one bond per patch (where a chain can have only one bond per patch). Compared to globular structures observed at $k_{\mathrm{B}}T = 1.0$, chain phases are stabilized by directional interactions and anisotropic bonding and therefore not an equilibrium structure, especially at higher temperatures.

[5.0 marks]

3. **Viscosity of a Lennard–Jones Fluid Using the Green–Kubo Method**

- **Step 1: Simulation time modification and density control**

  To simulate a Lennard–Jones fluid at the target number density

  $$\rho = \frac{N}{V} = 0.1,$$

  the simulation box dimensions and lattice parameters were adjusted accordingly. V can be calculated from the box size specified in the LAMMPS input file.

  The relevant section of the modified `LAMMPS` input file is shown below. To ensure numerical stability, the integration time step was chosen such that

  $$dt \ll 0.001.$$

  ```
  lattice          fcc 0.1

  variable dt equal 0.00001
  timestep 0.00001
  ```

  Reason or Justification: At larger time steps, particles that are initially placed close to one another, particularly due to periodic boundary conditions-can experience large repulsive forces, leading to numerical instability and poor energy conservation. To allow the system to relax smoothly from the initial configuration, a smaller time step ($dt = 10^{-5}$) was employed during the early stages of the simulation. This choice ensures stable integration of the equations of motion and prevents unphysical particle overlaps during equilibration.

  [5.0 marks]

- **Step 2: Box sizes and density control**

  The relevant section which led to the successful run is pasted below,

  ```
  region          box block 0 23 0 23 0 23
  create_box      1 box
  lattice         fcc 0.5
  ```

  Note: Here students should note that the correct value is **strictly not** as same as shown in this example. **The real test is whether students are able to find the relevant part which is causing problem, which has been pasted above.**

Reason or Justification: Due to periodic boundary condition the atoms can overlap as the box size is not the exact (integer) multiple of the lattice constant calculated for the given density and lattice structure (in case fcc). However, one of the simplest way is change the box size slightly within the range of lattice constant unless system stop blowing up.

In practical applications, due to the complexity associated with exact calculations, it is often more effective to adjust model parameters rather than pursue an exact solution, provided that the adjusted approach adequately captures the essential physical behavior of the system.

[**5.0 marks**]

- **Step 3: Density dependence of viscosity**
  The shear viscosity was computed for densities
  $\rho = 0.05, 0.1, 0.3, 0.4, 0.5$ using the Green–Kubo formalism.
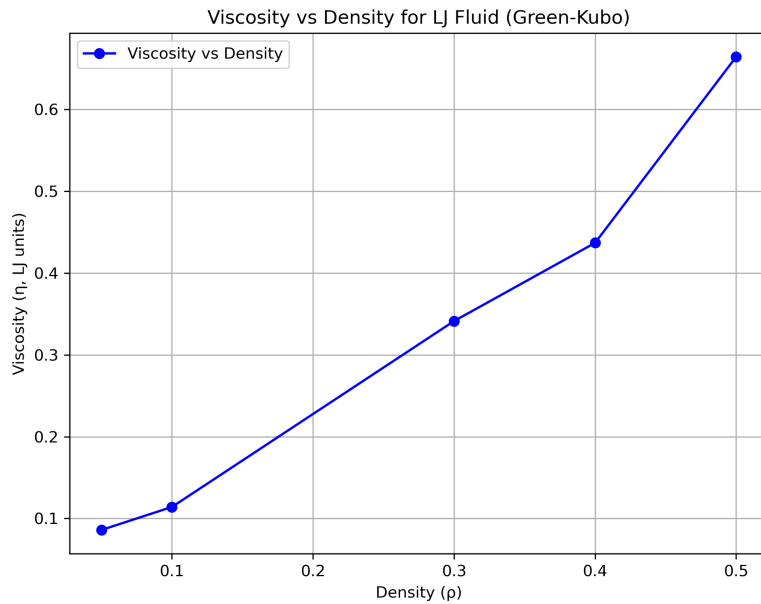

Figure 5: Viscosity as a function of density.

Figure-5 shows that viscosity increases monotonically with density.

This trend is physically reasonable, as higher densities lead to stronger interparticle interactions and enhanced momentum transport.

Note: Minimum three state points in the plot must be shown, for the full marks.

[**5.0 marks**]

- **Step 4: Conversion of viscosity from LJ to SI units**
  In Lennard–Jones (LJ) reduced units, viscosity is expressed in terms of the fundamental LJ units of mass m, energy ϵ, and length σ. The dimensional form of viscosity is

$$[\eta] = \frac{\text{mass}}{\text{length time}}.$$

In LJ units, the characteristic time scale is defined as

$$\tau = \sigma\sqrt{\frac{m}{\epsilon}}.$$

Therefore, the LJ unit of viscosity can be written as

$$\eta_{\mathrm{LJ}} = \frac{m}{\sigma\tau} = \frac{m}{\sigma^2}\sqrt{\frac{\epsilon}{m}} = \frac{\sqrt{m\,\epsilon}}{\sigma^2}.$$

Hence, the conversion factor from LJ viscosity units to SI units (Pa·s) is

$$\eta_{\mathrm{SI}} = \eta_{\mathrm{LJ}}\frac{\sqrt{m\,\epsilon}}{\sigma^2}.$$

(a) Substitution of physical values   The LJ parameters are mapped to physical units as follows:

$$\sigma = 1 \times 10^{-10}\,\mathrm{m},$$

$$\epsilon = k_{\mathrm{B}}T, \quad T = 300\,\mathrm{K},$$

$$k_{\mathrm{B}} = 1.380649 \times 10^{-23}\,\mathrm{J\ K^{-1}},$$

$$m = 12\,\mathrm{amu}, \quad 1\,\mathrm{amu} = 1.660539 \times 10^{-27}\,\mathrm{kg}.$$

First, convert the mass into SI units:

$$m = 12 \times 1.660539 \times 10^{-27} = 1.99265 \times 10^{-26}\,\mathrm{kg}.$$

Next, compute the energy scale:

$$\epsilon = k_{\mathrm{B}}T = 1.380649 \times 10^{-23} \times 300 = 4.14195 \times 10^{-21}\,\mathrm{J}.$$

Now evaluate $\sqrt{m\,\epsilon}$:

$$\sqrt{m\,\epsilon} = \sqrt{(1.99265 \times 10^{-26})(4.14195 \times 10^{-21})} = \sqrt{8.25 \times 10^{-47}} = 9.08 \times 10^{-24}.$$

Finally, divide by σ^2:

$$\frac{\sqrt{m\,\epsilon}}{\sigma^2} = \frac{9.08 \times 10^{-24}}{(1 \times 10^{-10})^2} = 9.08 \times 10^{-4}\,\mathrm{Pa}\cdot\mathrm{s}.$$

[2.5 marks]

(b) Final conversion factor

$$\boxed{1\ \eta_{\mathrm{LJ}} = 9.1 \times 10^{-4}\,\mathrm{Pa}\cdot\mathrm{s}}$$

Thus, the viscosity obtained from LAMMPS in LJ units can be converted to SI units by multiplying it with $9.1 \times 10^{-4}\,\mathrm{Pa}\cdot\mathrm{s}$.

[2.5 marks]

4. **Liquid–gas coexistence of the Lennard–Jones fluid at temperature $k_{\mathrm{B}}T = 0.7$**

   - **Step 1: Fitting procedure (slab simulation method)**
   The density profile obtained from the slab simulation is shown below. The profile is fitted to extract the coexistence densities of the liquid and gas phases.
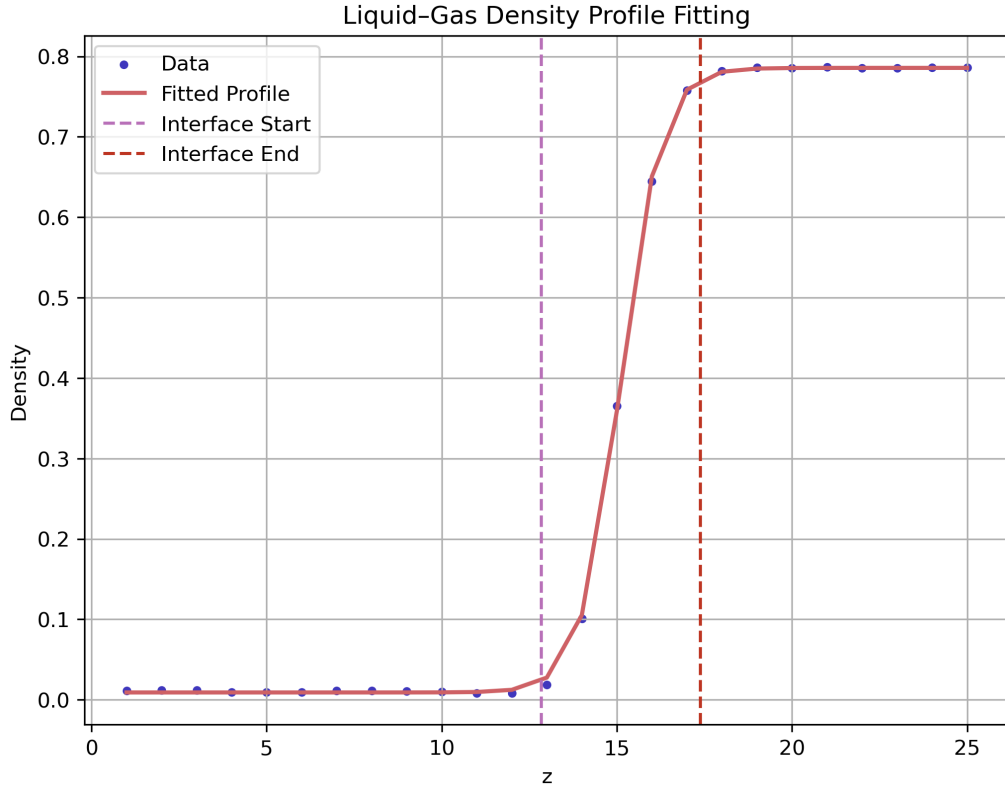
Figure 6: Fitted density profile for the Lennard–Jones fluid at temperature $k_{\mathrm{B}}T = 0.7$.

[15 Marks]

- **Step 2: Interface evolution with temperature**

  The coexistence densities obtained from the simulation are:

  – Liquid phase density: $\rho_l \approx 0.7856$

  – Gas (vapour) phase density: $\rho_g \approx 0.0091$

  The vapour phase corresponds to a low-density region. As the temperature increases, the vapour density increases while the liquid density decreases, leading to a reduction in the density contrast between the two phases. Consequently, the liquid–vapour interface becomes more diffuse, and the surface tension decreases with increasing temperature.

  [5 Marks]

5. **Martini Force-Field Representation of Carbon Nanotubes**

   - Since we have a chain configuration and each Martini carbon particle represents four real carbon atoms, the effective bond length between two Martini beads is approximately four times the real C–C bond length:

   $$d_{\mathrm{Martini}} \approx 4 \times 1.2 \text{ Å} = 4.8 \text{ Å}.$$

   This represents a configuration like (C-C-C-C-)(C-C-C-C-)(C-C-C-C-)(C-C-C-C-)(C-C-C-C-), corresponding to the given all atom configuration which looks like, C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-.

   [2.5 marks]

- On the provided graphene lattice (Fig. 7), Martini beads are placed such that each bead overlays four carbon atoms, forming a coarse-grained lattice that perfectly superimposes the real structure without voids or defects. To do so, there are several ways and each of them are correct answer.
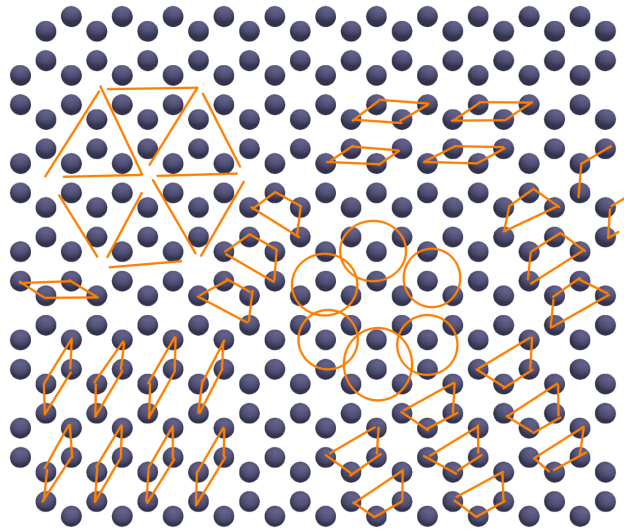

Figure 7: Graphene sheet with course grained lattice geometry, where each closed curve or atoms within the curve, represents a single Martini carbon atom.

[2.5 marks]