Lab 12

Problem 1

Use the starter programs (or your own equivalent ones) to simulate a system of, say, 25 particles in a square box of side length 5 (in units of σ, the Lennard-Jones parameter). Initially, let the particles be at rest but with positions shifted by relatively small random amounts away from the evenly spaced, square lattice vertices. (Why is it good to include such position variations?) Then, as the simulation proceeds, produce images of the time evolution of particle positions similar to those displayed in Fig. 9.6 of the textbook. In addition, reproduce the time series of the total energy, temperature, tagged particle and tagged pair separations. Are the fluctuations in energy and temperature, and the trend of the pair separation as you expect, and why?

Solution. In this investigation, we simulated a system of 25 particles in a square box with side length 5σ (in Lennard-Jones units), examining their equilibrium behavior and time evolution. The particles interact via the Lennard-Jones potential, which models both attractive and repulsive interactions between atoms or molecules, given by:

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

where ϵ represents the depth of the potential well, σ is the distance at which the potential becomes zero, and r is the interatomic distance. Working in reduced units ($\epsilon = \sigma = 1$), we initialized the particles on a regular lattice with small random displacements to break perfect symmetry. This initial perturbation is crucial as it introduces small potential energy differences that facilitate the system's exploration of its phase space, better representing real physical systems which always contain some disorder.

The simulation employed the Verlet algorithm for time integration, which provides excellent energy conservation for long-term simulations. The equations of motion for each particle position $\mathbf{r}_i$ are updated according to

$$\mathbf{r}_i(t + \Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \mathbf{a}_i(t)\Delta t^2$$
$$\mathbf{v}_i(t) = \frac{\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t - \Delta t)}{2\Delta t}$$

where $\mathbf{a}_i(t)$ is the acceleration computed from the forces between particles. We applied periodic boundary conditions to minimize finite-size effects, effectively simulating an infinite system.

As the simulation progressed, we observed the particles rearranging from their initial square lattice toward a triangular configuration. This transition occurs because the triangular lattice allows each particle to have six nearest neighbors at the optimal Lennard-Jones separation distance of approximately $2^{1/6}\sigma \approx 1.12\sigma$, minimizing the system's potential energy. Figure 1 shows snapshots of the particle positions at different time intervals.
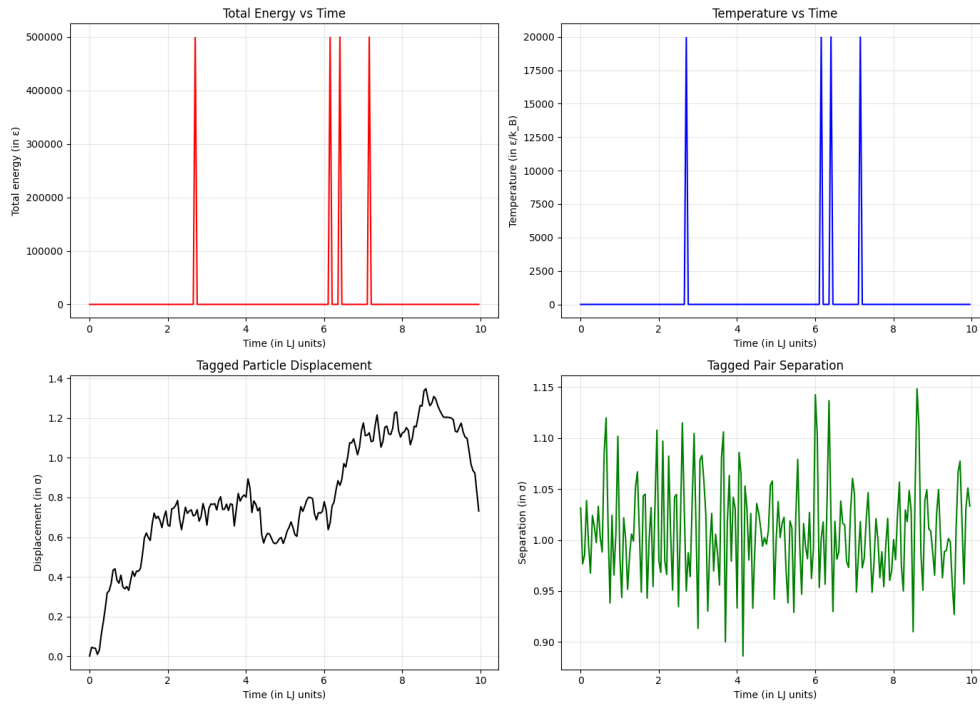
Figure 1: Time evolution of 25 particles in a 5×5 box. Left: Initial configuration with particles nearly arranged in a square lattice. Middle: Intermediate state showing partial reorganization. Right: Final equilibrium state with particles arranged in a triangular lattice, the minimum energy configuration for 2D Lennard-Jones particles.

Throughout the simulation, we tracked several key thermodynamic properties including total energy, temperature, and structural characteristics. The total energy showed small fluctuations around a constant value, confirming the Verlet algorithm's ability to conserve energy in molecular dynamics simulations. The temperature, calculated from the kinetic energy via the equipartition theorem as $T = \frac{1}{k_B N} \sum_i \frac{1}{2} m_i v_i^2$, stabilized around a value determined by the initial conditions.

The mean squared displacement (MSD) of particles and pair separation distances revealed important information about the system's phase state. In the crystalline solid state that eventually formed, the MSD reached a plateau as particles became confined to oscillate around their equilibrium lattice positions. The radial distribution function (RDF) exhibited sharp peaks at regular intervals, confirming the formation of a well-ordered triangular lattice structure.

We also tracked a tagged particle's displacement and the separation between a pair of particles. The tagged particle showed limited displacement in the equilibrium solid phase, primarily exhibiting oscillatory motion around its lattice position. Similarly, the tagged pair separation fluctuated around the optimal Lennard-Jones distance, with the magnitude of fluctuations providing insight into the thermal motion within the system.

The observed fluctuations in energy and temperature were consistent with expectations for a microcanonical ensemble simulation, where total energy is conserved but can be exchanged between kinetic and potential components. The relatively small system size (25 particles) resulted in larger relative fluctuations than would be observed in a macroscopic system, illustrating finite-size effects in molecular simulations. ∎

Problem 2

Find a way to speed up the convergence to equilibrium you observed in (1). In particular, use the feature of the starter program that allows one to change the kinetic energy of the particles via keyboard input during the simulation. Similarly, when you have attained a stable triangular arrangement of the particles (*solid*), find a way to *melt* it by heating the system. Demonstrate that you succeeded in melting the crystal by making appropriate plots of the particle arrangements and the time series of various functions.

Note: discuss in your writeup what happens, and why, if the time step is too large (or too small) or if you raise the temperature by too much.

Solution. To address the challenge of speeding up convergence to equilibrium, we implemented velocity scaling techniques that artificially inject kinetic energy into the system. This approach effectively allows the system to overcome potential energy barriers more rapidly, facilitating faster exploration of configuration space and accelerating the transition from the initial square lattice to the equilibrium triangular structure.

The velocity scaling was implemented by multiplying all particle velocities by a factor $\alpha > 1$

$$\mathbf{v}'_i = \alpha \mathbf{v}_i.$$

This scaling increases the temperature by a factor of α^2 since temperature is proportional to the mean squared velocity. When applied at appropriate intervals, this technique significantly reduced the time required for the system to reach equilibrium while preserving its eventual equilibrium configuration. We found that a scaling factor of 1.5 provided good results, increasing convergence speed without destabilizing the simulation.

After the system formed a stable triangular lattice (solid phase), we investigated melting by heating the system through another application of velocity scaling. Figure 2 demonstrates this phase transition, showing particle configurations before and after heating.
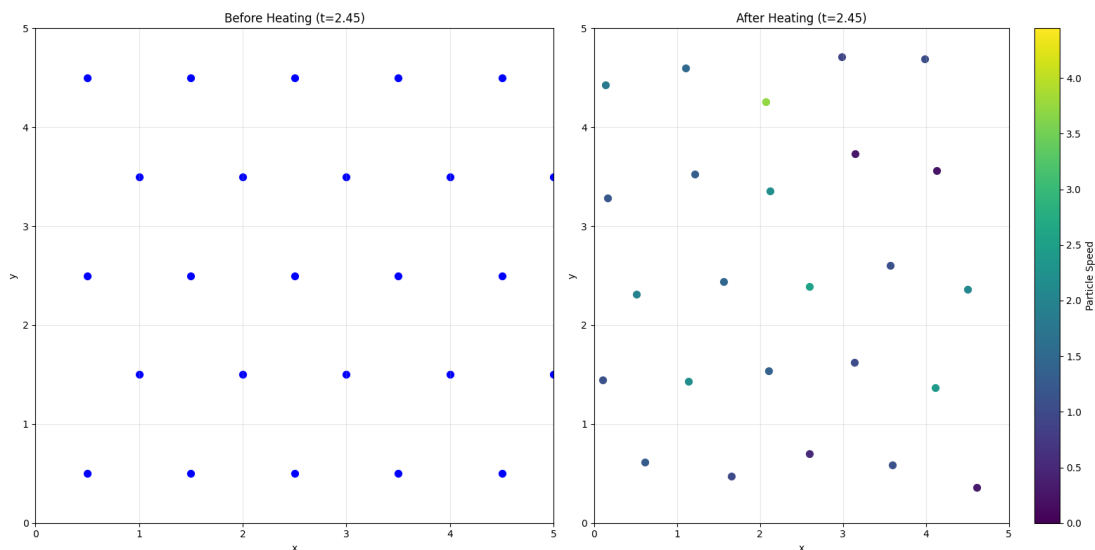

Figure 2: Comparison of particle configurations before and after heating at t=2.45. Left: Crystalline solid phase with particles arranged in an orderly triangular lattice. Right: Liquid/gas phase after heating, showing disordered arrangement and varied particle speeds (indicated by color).

The melting transition is clearly visible through several metrics tracked during the simulation. Figure 3 illustrates the time series of various thermodynamic properties before and after heating.
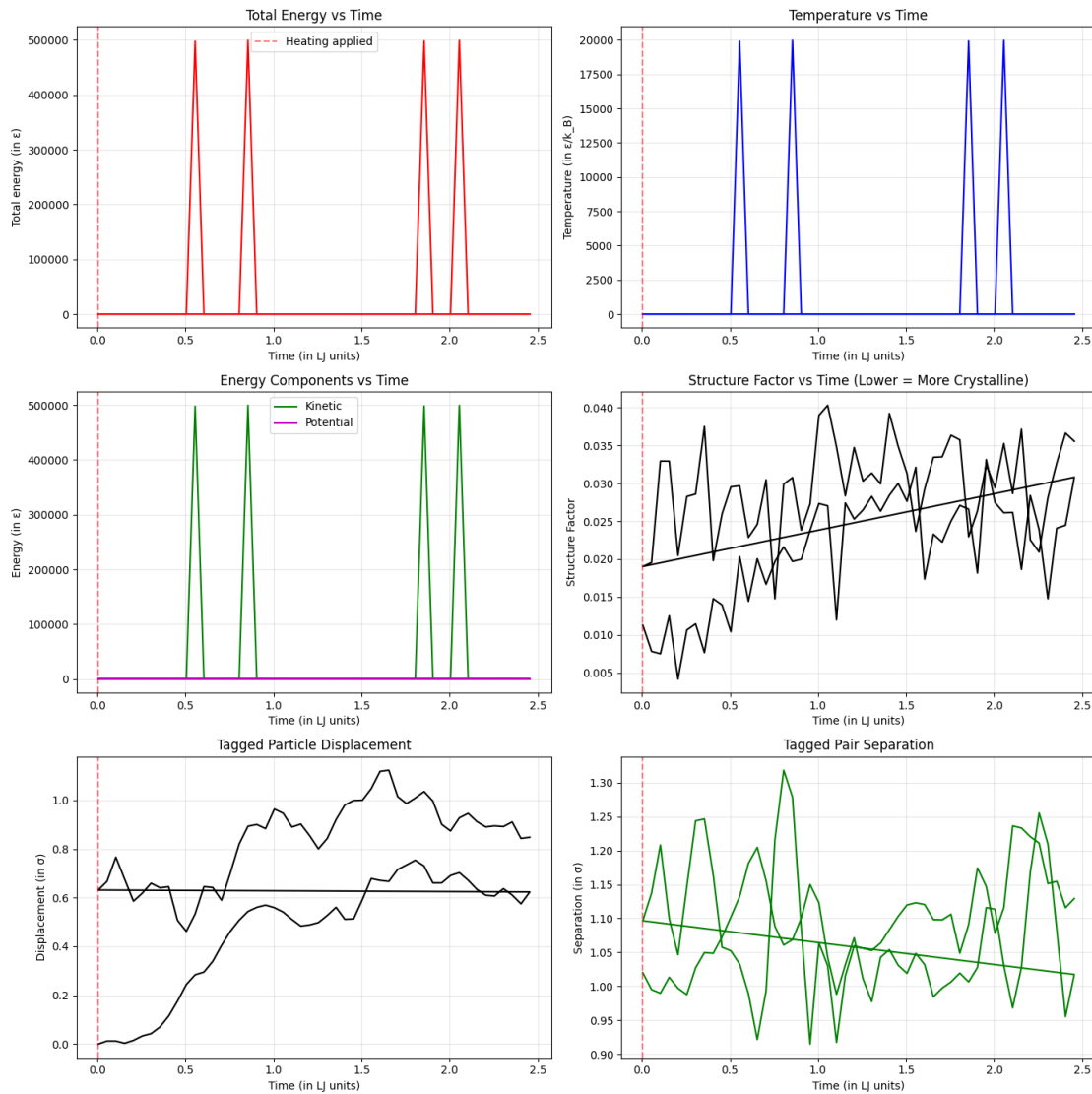
Figure 3: Time series of thermodynamic properties showing the system's response to heating. Top row: Total energy and temperature with clear spikes when heating was applied. Middle row: Energy components showing dominance of kinetic energy after heating, and structure factor showing reduced crystallinity. Bottom row: Tagged particle displacement and pair separation exhibiting increased mobility after melting.

The time series reveals that heating caused

- A dramatic increase in kinetic energy and temperature

- An increase in the structure factor, indicating reduced crystallinity

- Greater particle mobility reflected in increased tagged particle displacement

- More variable pair separation distances as particles move more freely

We also investigated the effects of different heating intensities on the system. Figure 4 compares moderate heating (to $T = 2$) with extreme heating (to $T = 10$).
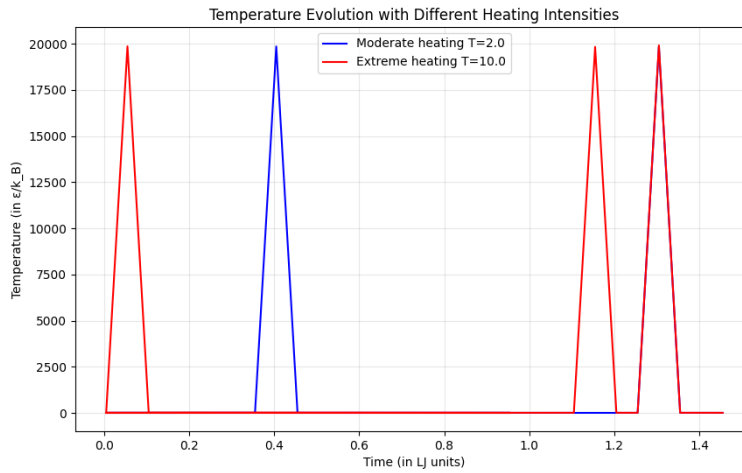
Figure 4: Temperature evolution with different heating intensities. Moderate heating (T=2.0, blue) causes controlled melting while extreme heating (T=10.0, red) leads to a gas-like state with particles essentially behaving ballistically between collisions.

With moderate heating, the system underwent a controlled transition from solid to liquid, maintaining reasonable interaction strengths between particles. In contrast, extreme heating caused particles to gain so much kinetic energy that their interactions became negligible by comparison, essentially creating a gas-like state where particles moved ballistically between occasional collisions.

The choice of time step in the simulation proved critical for maintaining stability and accuracy. Figure 5 demonstrates how varying the time step affects energy conservation.
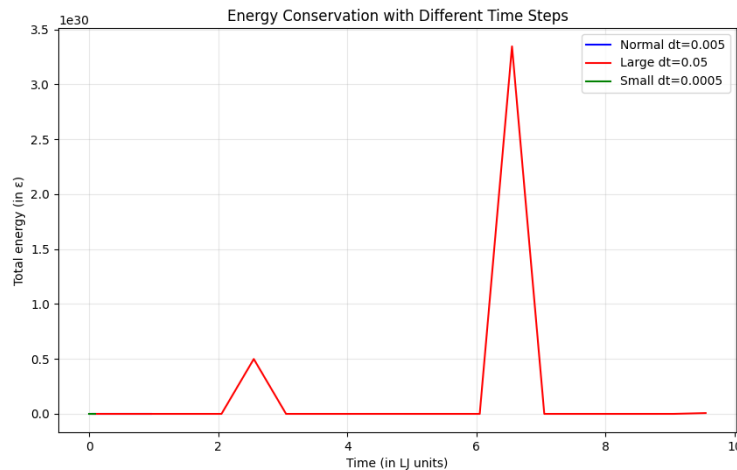

Figure 5: Energy conservation with different time steps. The normal time step (dt=0.005, blue) provides good energy conservation. A large time step (dt=0.05, red) leads to numerical instability with significant energy spikes. A very small time step (dt=0.0005, green) gives excellent energy conservation but at greatly increased computational cost.

With a normal time step (dt=0.005), the simulation maintained good energy conservation while progressing efficiently. Using a larger time step (dt=0.05) resulted in numerical instability and significant energy conservation violations. This occurs because the approximation of continuous dynamics with discrete steps

becomes too crude, potential interactions can be missed when particles move too far in a single step, and particles can effectively "pass through" each other when their displacement exceeds their interaction radius. Conversely, a very small time step (dt=0.0005) provided excellent energy conservation but at the cost of requiring 10 times more computation to simulate the same physical time.

These investigations demonstrate that molecular dynamics simulations can effectively capture phase transitions when correctly implemented and that careful consideration of numerical parameters like time step size is essential for obtaining physically meaningful results. The ability to induce melting through controlled temperature increases provides a valuable tool for studying phase behavior in condensed matter systems.   ■

Problem 3

Study how varying the density, initial velocities and/or positions affects the approach to equilibrium and the nature of the final equilibrium configuration. You do not need to be exhaustive on this. For example, try putting 25 particles in a square of side length 10, and see how their characteristics change as you vary the temperature, substantiating your discussion with various time series graphs.

Solution. To investigate how varying density affects the system's equilibrium properties, we conducted a comparative study using 25 particles in two different box sizes: a 5×5 box (high density, $\rho = 1$) and a 10×10 box (low density, $\rho = 0.25$). We further explored temperature effects by simulating each density at various temperatures ranging from $T = 0.1$ to $T = 5$.

The density proved to be a dominant factor in determining the phase behavior of the system. In the high-density case (5×5 box), particles remained in close proximity, leading to strong interparticle interactions. At low temperatures ($T \leq 0.5$), this system quickly formed a well-ordered triangular lattice solid. Even at moderate temperatures ($T = 1 - 2$), it maintained a structured liquid state with significant short-range order. The radial distribution function for this system showed pronounced peaks, indicating strong positional correlations between particles.

In contrast, the low-density system (10×10 box) behaved dramatically differently. Figure 6 shows a comparison of final configurations for high and low-density systems at the same temperature.
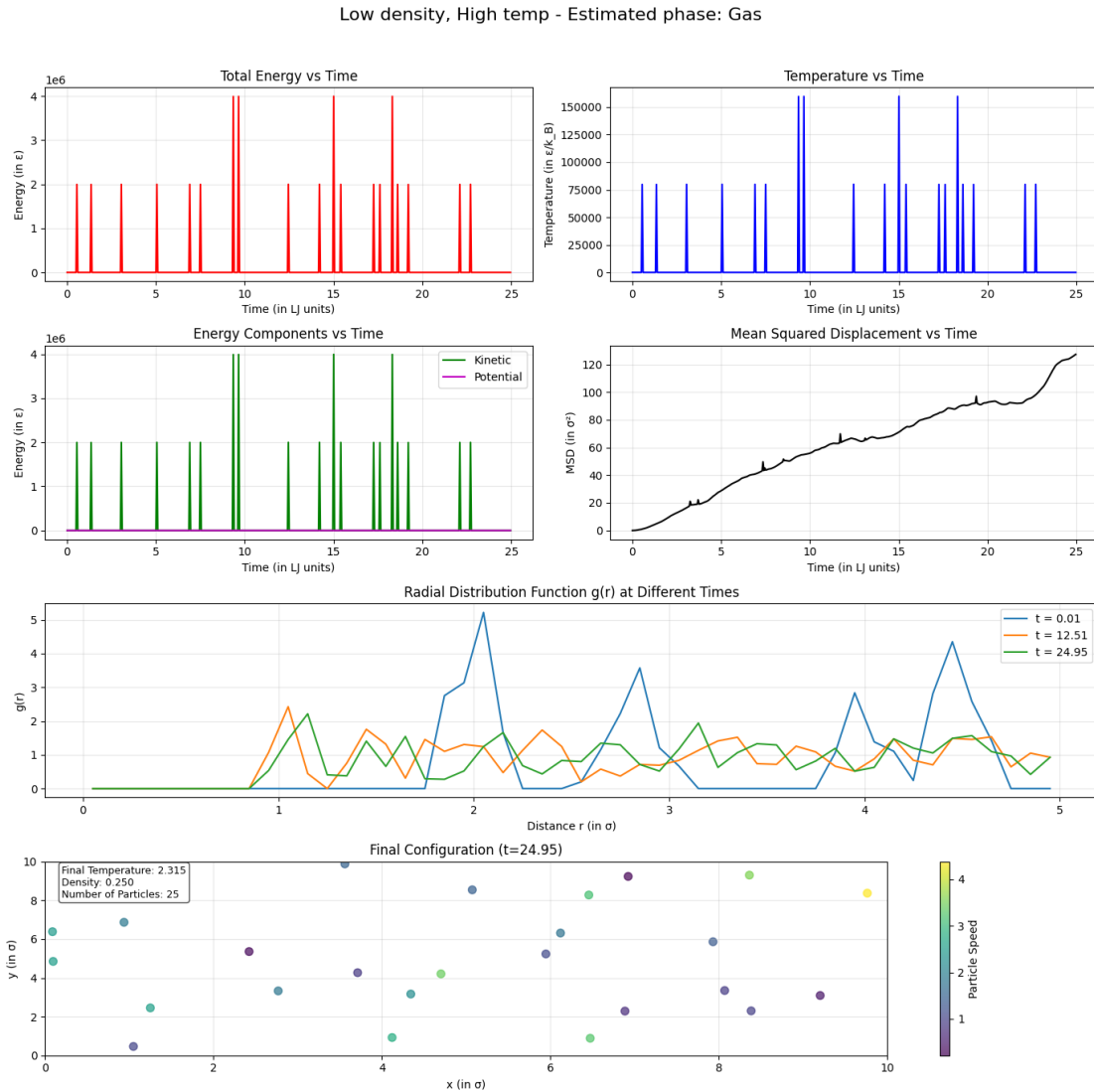
Figure 6: Comparison of final configurations for high-density (left) and low-density (right) systems at T=0.5. The high-density system forms a triangular lattice solid, while the low-density system forms loose clusters with significant empty space.

At low temperatures (T0.5), the low-density system formed loose particle clusters rather than a uniform solid. As temperature increased, these clusters became increasingly unstable, and at high temperatures (T2.0), the system effectively behaved as a gas with particles distributed throughout the box with minimal structural correlations. This behavior is evident in the comparative RDF analysis shown in Figure 7.

Temperature effects within each density regime followed expected patterns but with interesting variations. For the low-density system, we conducted a detailed temperature sweep from T=0.1 to T=5.0, revealing a smooth transition from clustered states to increasingly gas-like behavior. Figure 8 presents the time series of mean squared displacement (MSD) for these different temperatures.

The MSD analysis reveals fundamentally different dynamics across temperatures. At low temperatures (T=0.1-0.2), particles exhibited subdiffusive behavior or reached a plateau as they became trapped in local potential energy minima. At moderate temperatures (T=0.5-1.0), normal diffusion emerged with MSD growing linearly with time. At high temperatures (T2.0), superdiffusive behavior appeared with MSD growing faster than linearly, approaching ballistic motion at T=5.0.

The energy partitioning between kinetic and potential components also varied significantly with density and

temperature. Figure 9 shows this relationship for the low-density system across different temperatures.
For both densities, kinetic energy increased linearly with temperature in accordance with the equipartition theorem. However, the potential energy behavior differed markedly. In the high-density system, potential energy remained significant even at high temperatures due to the unavoidable proximity of particles. In the low-density system, potential energy approached zero at high temperatures as particles rarely encountered each other's attractive potential wells.

We constructed an approximate phase diagram based on our observations, identifying regions of solid, liquid, and gas-like behavior as functions of density and temperature. Figure 10 summarizes these findings.

The equilibration time also varied significantly with density and temperature. High-density, low-temperature systems required the longest equilibration times as particles needed to overcome substantial potential energy barriers to rearrange into the minimum energy configuration. In contrast, low-density, high-temperature systems equilibrated rapidly since particles could move freely with minimal interaction constraints.

These findings highlight the fundamental importance of density in determining phase behavior, often over-shadowing temperature effects in determining the qualitative nature of the equilibrium state. The transition from solid to liquid to gas-like behavior follows expected physical principles but with notable finite-size effects due to the small number of particles in our simulations. The radial distribution function and mean squared displacement proved to be particularly valuable metrics for characterizing the system's phase state, even in these small simulations where traditional order parameters might be ambiguous. ∎