Methods of Computer Simulation

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1   Introduction

These results were calculated from a molecular dynamics simulation using a Lennard-Jones potential and reduced units (energy measured in ϵ, distance measured in σ) in a microcanonical ensemble (NVE). 172 particles were used in a cube of length 6 σ to give a system density of 0.796 m^{-3} . The temperature (measure in ϵ) was held constant for each simulation using velocity scaling. A time step of 5 ms was used and the system was run for 2 s (400 steps) to equilibrate before any measurements were taken.

The operation of a thermostat or barostat coupled to the dynamics of the molecules may change the positions and velocities in non-mechanical ways, which can influence the values of the calculated MSD(t) and VCF, although this effect will be significantly reduced in equilibrated systems.
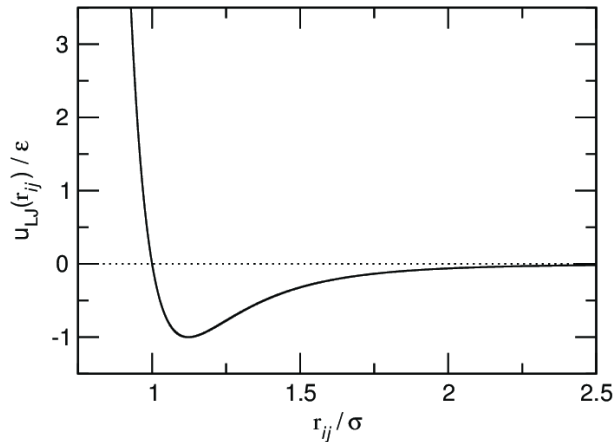

Figure 1: A normalised Lennard-Jones Potential

2   Mean Squared Deviation

The mean squared displacement (MSD) is defined as

$$MSD(t) = \frac{1}{N} \sum_{i=1}^{N} |\mathbf{r}_i(t) \cdot \mathbf{r}_i(0)|^2 = \left\langle \Delta \mathbf{r}(t)^2 \right\rangle \tag{1}$$

Before their first collision, particles on average will move in straight lines. This is called ballistic motion. For non-interacting particles in ballistic motion, the MSD is proportional to t^2. Once particles are interrupted by collisions, at longer times, the collisions lead to diffusive motion. This can be used to determine the diffusion constant D.

$$\left\langle \Delta \mathbf{r}(t)^2 \right\rangle = 6Dt \tag{2}$$

The change between ballistic and diffusive motion can be shown on log-log plot by a decrease

in gradient. The change-over is not sharp, but happens on the timescale of the typical interval between collisions. This can be seen in Fig. 2 at approximates 1 s.
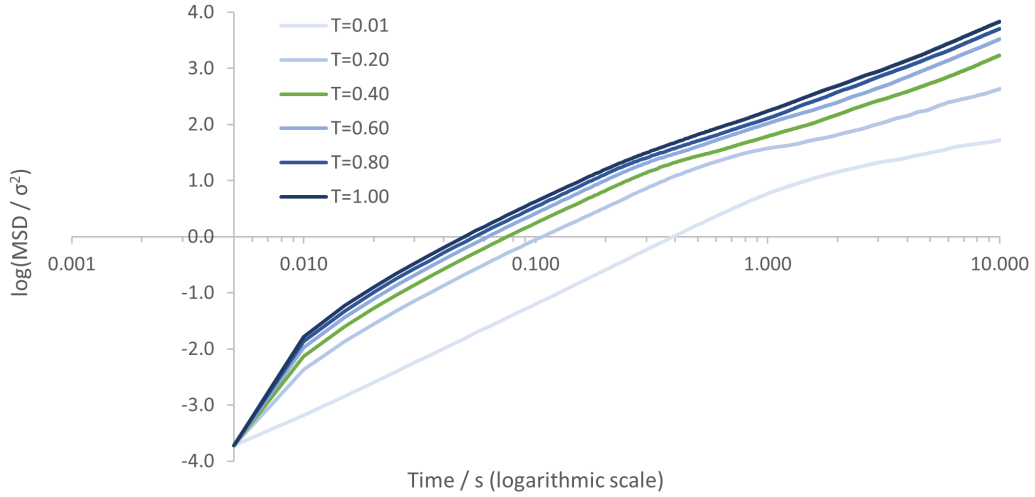

Figure 2: A log-log plot of MSD and time to demonstrate the shift between ballistic and diffusive motion within the system.

Using Eqn 2, the diffusion constant can be calculated for each temperature.

	T=0.01	T=0.20	T=0.40	T=0.60	T=0.80	T=1.00
Ballistic Gradient	0.8671	0.9171	0.9317	0.9387	0.9370	0.9364
Diffusive Gradient	0.3064	0.4808	0.7366	0.7356	0.7544	0.7690
Diffusion Constant	0.05107	0.08013	0.12277	0.12260	0.12573	0.12817

Table 1: Ballistic motion was calculated from $t = 0.010 - 0.200s$. Diffusive motion was calculated from $t = 5 - 10s$. All values are given in $\sigma^2 s^{-1}$.

The gradient decreases in diffusive motion as expected. The difference between the gradients is less than the factor of 2 that would be seen for non-interacting particles due to the L-J potential in the system.

3   Velocity Autocorrelation Function

The time variation of the velocity autocorrelation function (VCF) represents an average behaviour for the collisions in the system at the given temperature and density conditions and is defined as

$$VCF = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle \tag{3}$$

The normalised VCF $Z(t)$ is also often given

$$Z(t) = \frac{\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle}{\langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle} \qquad (4)$$

After the equilibration period, multiple times of origin were used (t=2, t=4, t=6) and all sequences were averaged to give a trajectory averaged VCF. This, in addition to increasing the sample size (number of particles) used in calculating the VCF results in smaller statistical fluctuations.
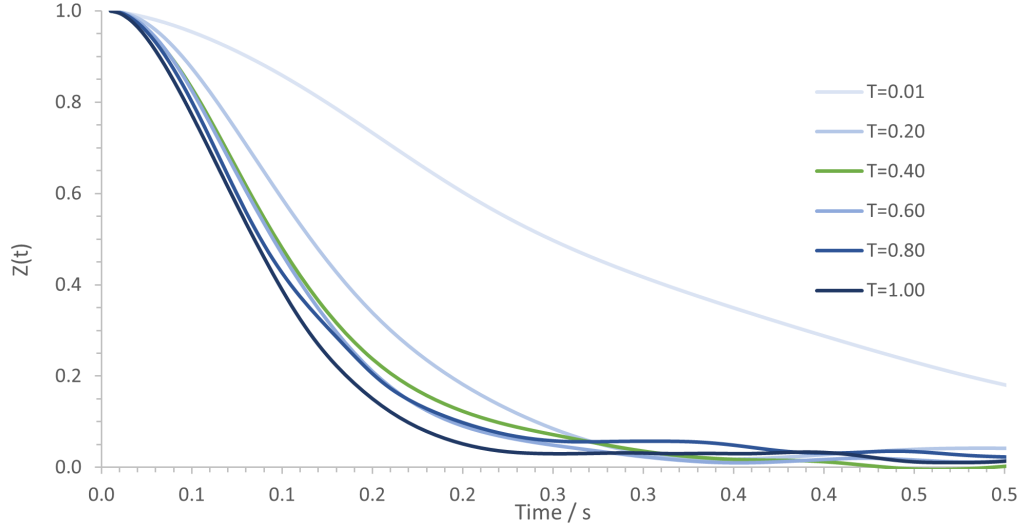

Figure 3: A plot of the normalised VCF for varying temperatures. The relaxation time for all temperatures (excluding T=0.01) is approximately 0.40 s.

The initial values of VCF increased proportionally with temperature as would be expected. The VCF decays to zero as motion of particles becomes randomised through collisions, with the highest temperatures decaying fastest due to a higher collision frequency.
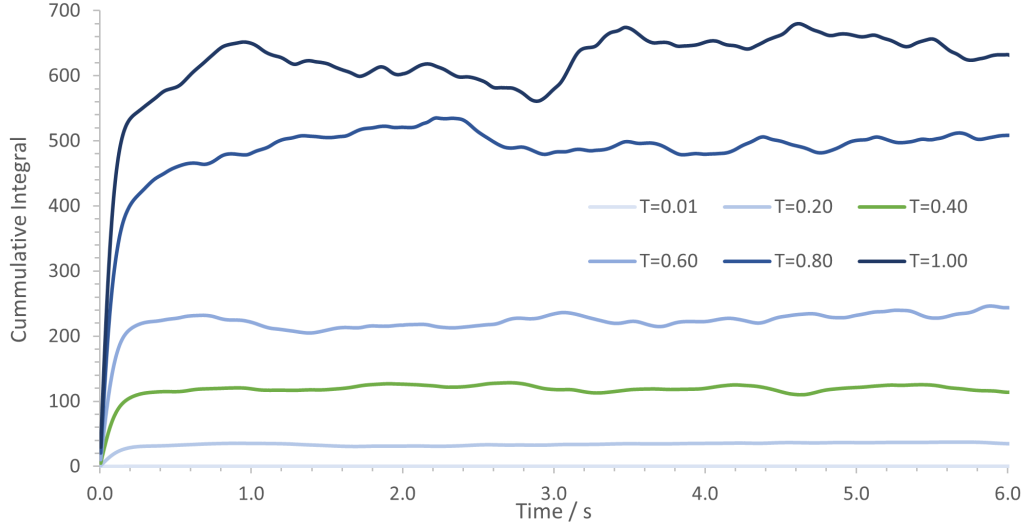
Figure 4: The cumulative integral= $\int_0^t \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle dt$ of VCF for each temperature.

As the kinetic energy is higher at larger temperatures, the fluctuations in Fig. 4 increase with temperature. This could be reduced further by including more times of origin to average over. As $t \to \infty$, the cumulative integral of the VCF tends towards the value of the diffusion constant for that temperature.

$$D = \int_0^\infty \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle dt \tag{5}$$

	T=0.01	T=0.20	T=0.40	T=0.60	T=0.80	T=1.00
Cumulative Integral	0.3091	36.4444	120.1205	232.3112	497.5021	651.7781
Diffusion Constant	0.1030	12.1481	40.0402	77.4371	165.8340	217.2594

Table 2: Cumulative integral values were calculated using the average cumulative integral between $t = 4 - 6s$. All values are given in $\sigma^2 s^{-1}$.

4   The Diffusion Constant

The diffusion constant, D can be derived to be

$$D = D_0 e^{-Q/k_B T} \tag{6}$$

where Q is the activation energy for diffusion and D_0 is the diffusion coefficient at infinite temperature.
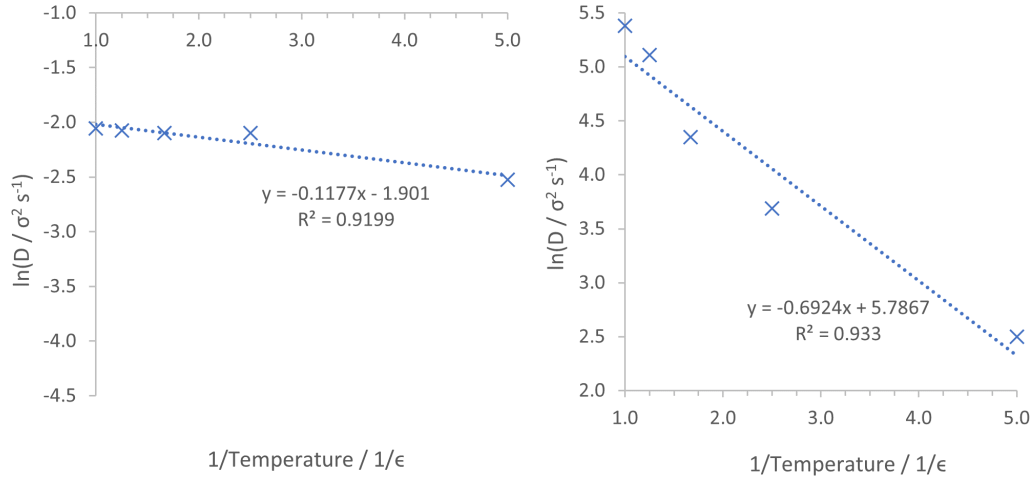
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Figure 5: An Arrhenius plot of diffusion values calculated from the MSD (left) and VCF (right). T=0.01 is not included.

The MDS and VCF give drastically different values for the diffusion constant with those from the VCF being 3 orders of magnitude higher. Despite the difference in values both sets of values are in reasonable agreement with Eqn 6 (Fig. 5) with R^2 values of above 0.9 for each.