A Correction to the Equipartition Theorem by the Lennard-Jones Potential

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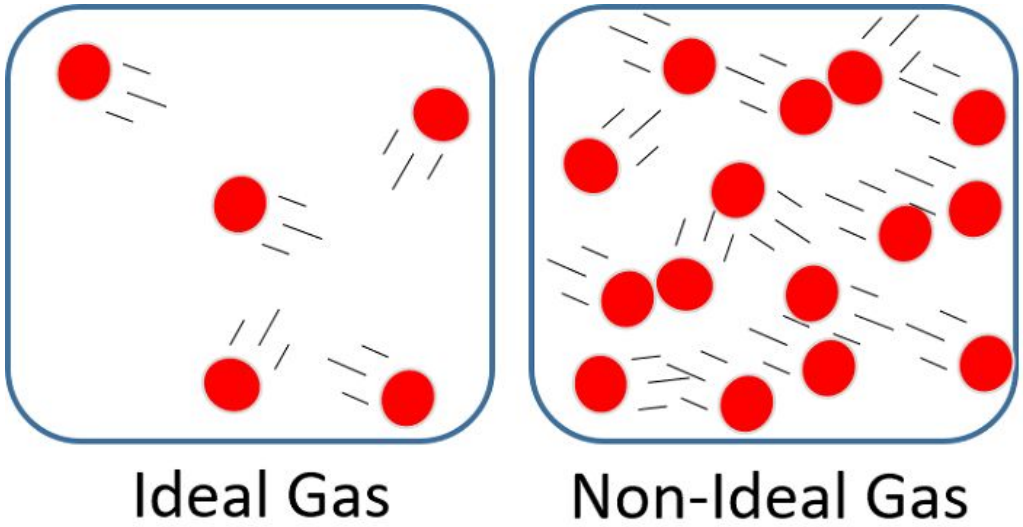
Motivation - Gases Are Not Always Ideal

- Ideal Gas: Inter-particle forces are not significant
- Ideal Gas: High-Temperature/Low Density



Partition Function of Non-Ideal Gas

- Reduces to two partition functions
- U = potential energy
- Zc, integral over all possible configurations of N particles
- True for all density/temperature

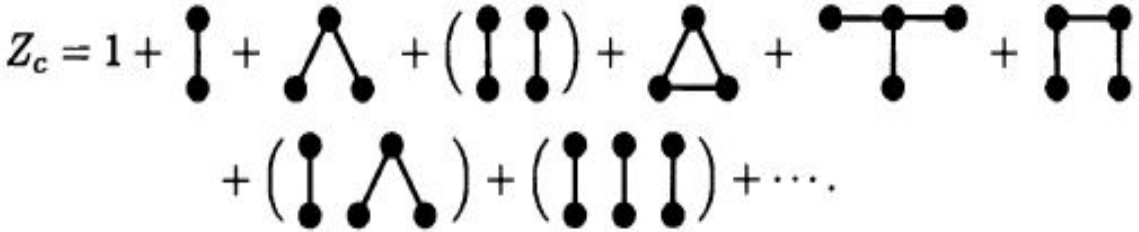
$$Z = \frac{1}{N!}\left(\frac{\sqrt{2\pi mkT}}{h}\right)^{3N} \int d^3r_1 \cdots d^3r_N \, e^{-\beta U_{\text{pot}}}$$

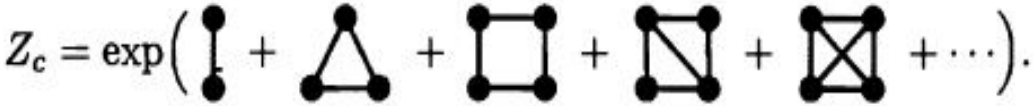
$$= Z_{\text{ideal}} \cdot \frac{1}{V^N} \int d^3r_1 \cdots d^3r_N \, e^{-\beta U_{\text{pot}}},$$

$$Z_c = \frac{1}{V^N} \int d^3r_1 \cdots d^3r_N \, e^{-\beta U_{\text{pot}}},$$

Cluster Expansion

- Rewrite Zc as diagrammatic perturbation series
- Each diagram represents a cluster of simultaneously interacting molecules
- At low density the second expression is well behaved





The Lennard-Jones Potential

$$u(r) = u_0\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right].$$

- Basic model for pairwise interactions
- Very repulsive at short distances <= r0
- Slightly attractive at further distances
- r0 roughly the diameter of a molecule
- u0 depth of potential well, or strength of attraction/repulsion

The Lennard-Jones Potential

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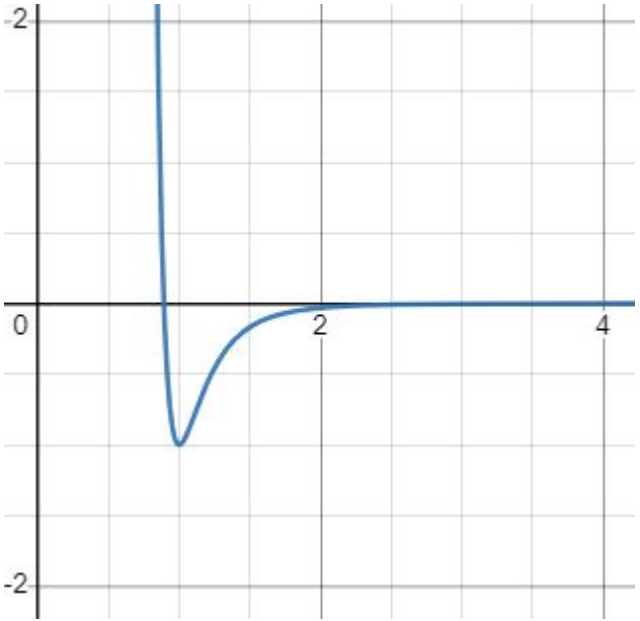
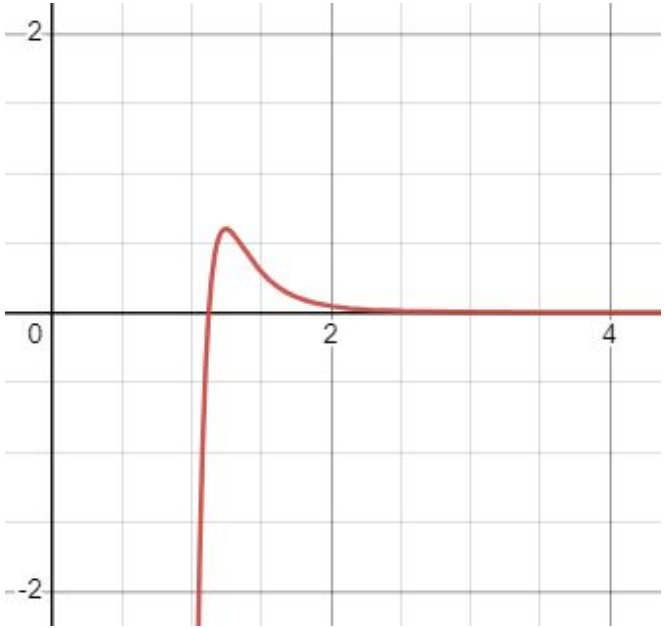
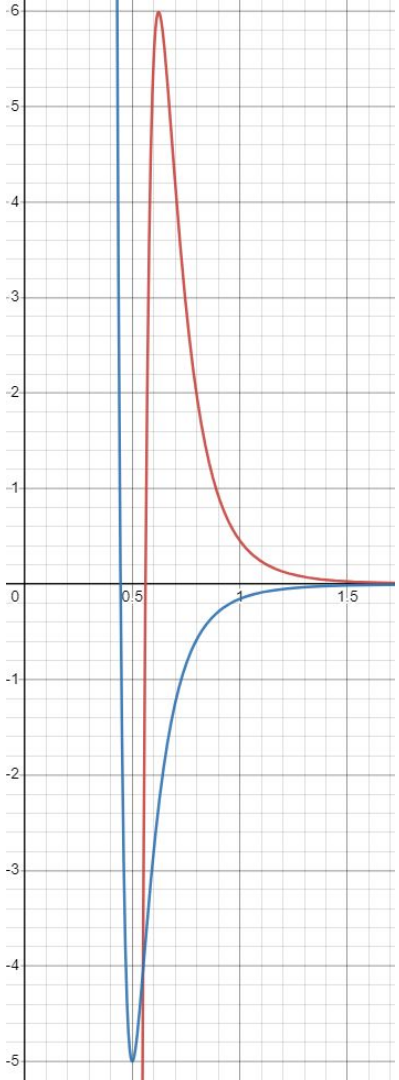


(Potential)



(Force)



Problem

Is there a correction to the ideal gas internal energy when adding pairwise interactions by the Lennard-Jones potential? And if so what is the sign of this correction and how do variables of the simulation affect the significance of this correction?

$$KE_{avg} = \frac{3}{2}kT \quad \text{per molecule}$$

k = Boltzmann constant = R/N_A

$$k = 1.38066x10^{-23} J / K$$

$$KE_{avg} = \frac{3}{2}RT \quad \text{per mole}$$

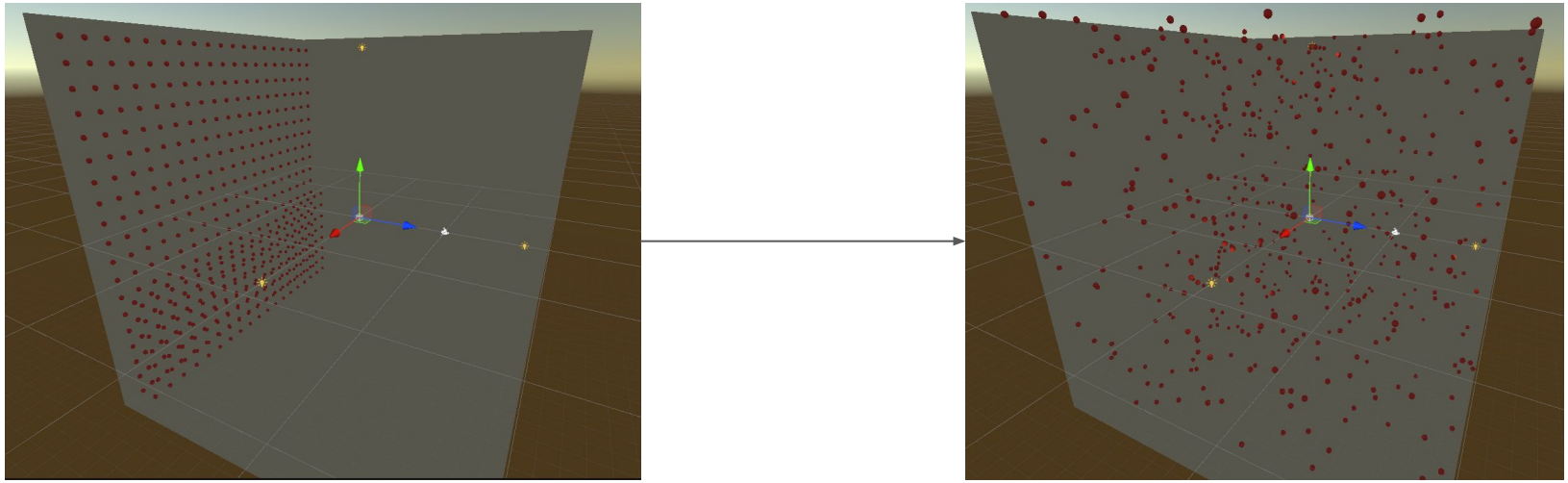
R = universal gas constant = kN_A

$$R = 8.3145 J / mol\ K$$

Solution

$$Kinetic\ Energy = U_{tot} + U_{pot}$$

- At time t < 0 the particles are far apart and static. (Non-Interacting)
- At time t = 0 the particles are given random initial kinetic energy.
- At time t > 0 the particles interact through some negative potential energy.



t < 0

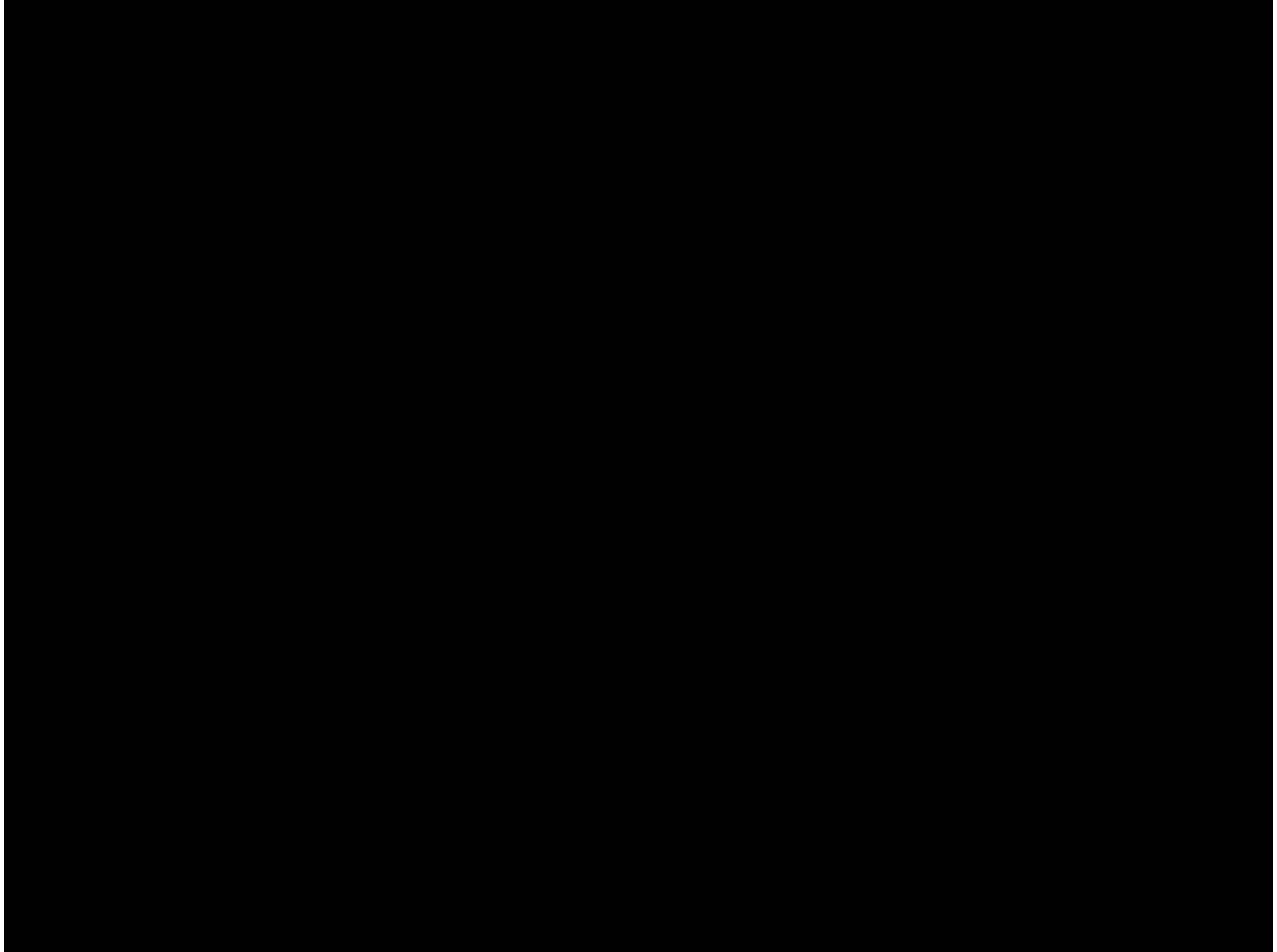
t > 0

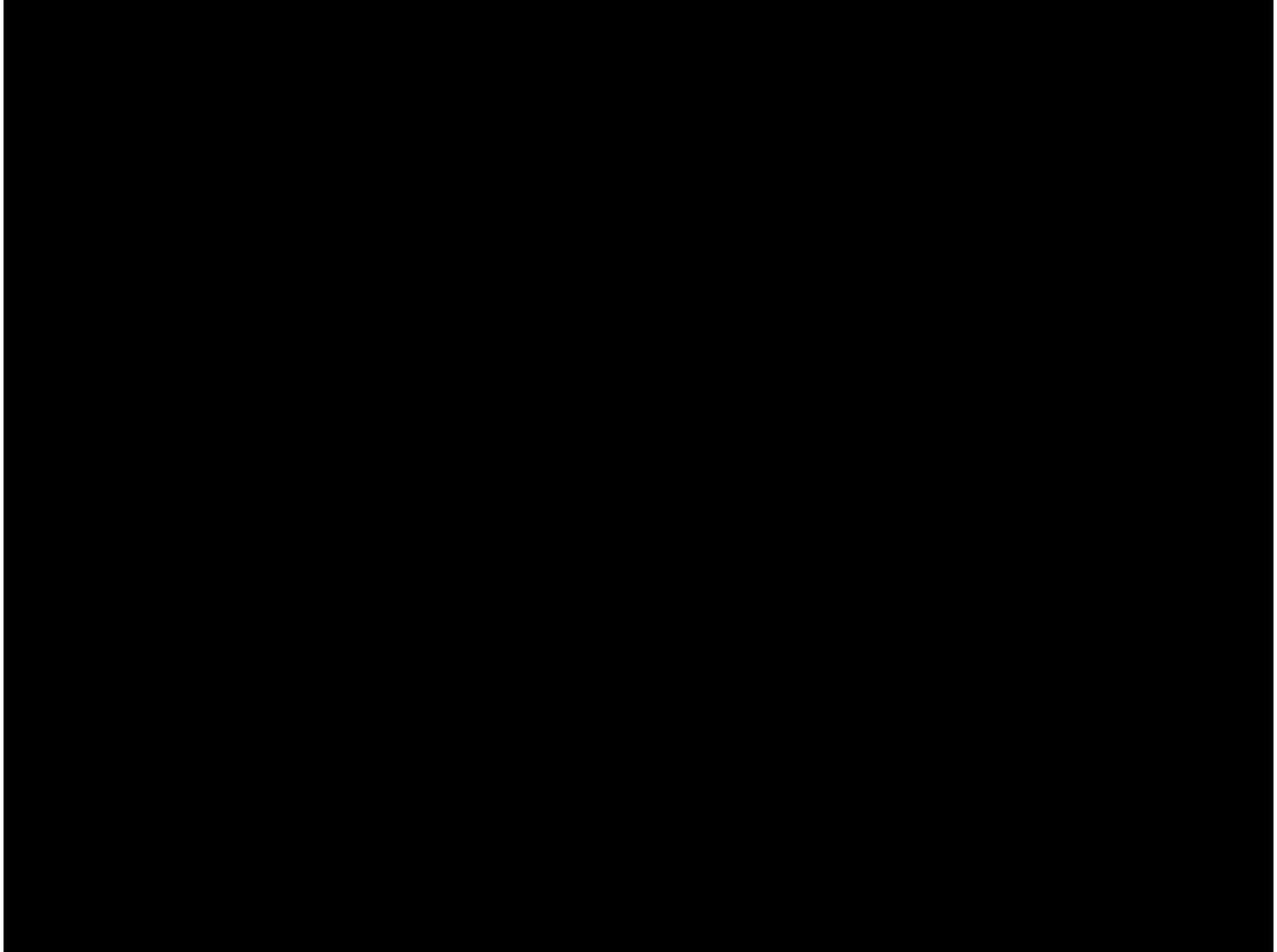
Trial #:	Total Energy:	Potential Energy:	Kinetic Energy:
1	998.4315	-37.31397	1035.745
2	998.8915	-34.51808	1033.41
3	1001.637	-26.3421	1027.979
4	999.1211	-34.13357	1033.254
5	1002.51	-23.43491	1025.945

(Note: each of these values are averages over continuous calculations for 2 seconds)

There is an increase in total kinetic energy!

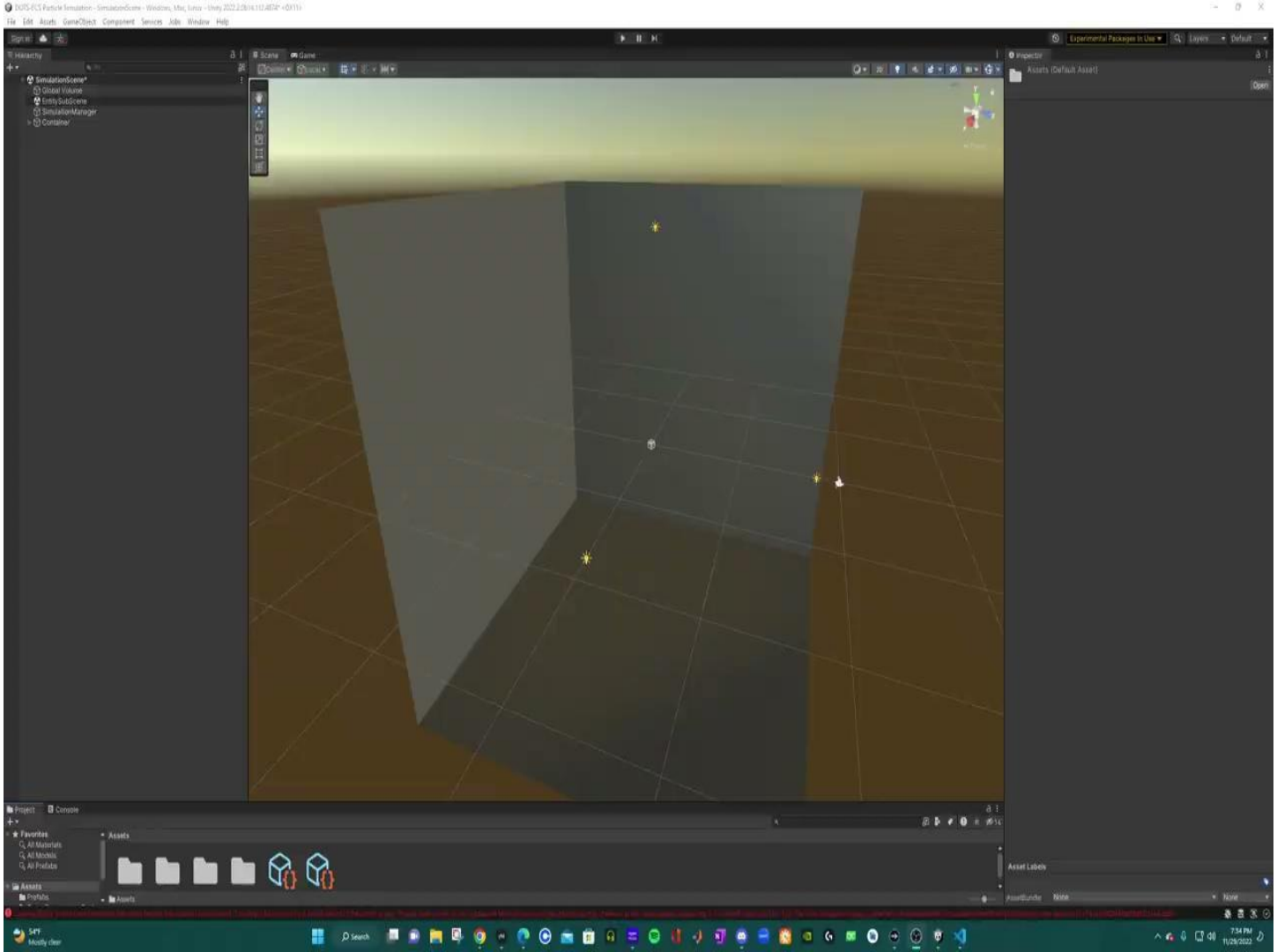
- This corresponds to only a 3% correction of the kinetic energy.
- However, our simulation can only hold accuracy at low temperature/energy which means that this is a correction of 3% at approximately an initial temperature of 0.00016K.





Higher Energies

At higher energies the correction becomes much less significant! This simulation is at 10x the energy of the first and only has a correction of about 0.04% to the kinetic energy.



Thank you!