

# The Correction to the Equipartition Theorem by The Lennard-Jones Potential

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Group  $\psi 1$

Yes, willing to present and you can post.

## Motivation

In this class we have so far only considered the dynamics of ideal systems, where each of the individual unit components do not interact with one another. In these cases we have been able to show how extensive and intensive properties of the system arise from the statistical mechanics, such as the entropy, specific heats, etc.. We are also able to mathematically prove why certain formulas apply to the macroscopic quantities of the systems, from the microscopic properties of the components.

However real life is not so simple, and most systems of particles have some interaction between the particles themselves. This usually means that we cannot calculate the properties of these systems exactly from the microscopic components, and we must make approximations.

Therefore in order to analyze real systems at a desired precision, we must choose a suitable approximation to model internal interactions, and the effect they have on the macroscopic properties.

For example in real life there is no such thing as a perfectly ideal gas, as there are almost always some forces between the gas particles. Finding a good model for this behavior is useful in many situations such as quantitatively predicting the condensation of a dense gas, or predicting the behavior of gasses at lower temperatures, or higher densities. These forces mean that in a non-ideal gas there is a potential energy term described by the attractive and repulsive interactions of the particles, alongside the kinetic energy associated with their movement. This represents an additional correction to the equipartition theorem, which only describes the energy of a gas in terms of a sum of the kinetic energies of the individual particles. When only considering pairwise interactions an approximation to this potential energy is called the Lennard-Jones potential.

$$u(r) = u_0[(r_0/r)^{12} - 2(r_0/r)^6]$$

Where this equation represents a potential between a pair of particles. But how significant is this correction in a large gas?

## Background Info

This correction term is relatively simple. This is because it is derived in the low-density limit in ch 8, however within this limit it is quantitatively accurate, unlike any model we have worked on so far.

In this low-density limit, Schroeder attempts to find the effects of these interparticle interactions though analyzing the partition function, and finds there is a correction factor  $Z_c$  that is an integral over all configurations of the gas molecules representing these intermolecular interactions. It turns out we can represent this integral through a diagrammatic expansion, a sum of integrals where each integral represents a set of 1, 2, ... N molecules interact with 1, 2, ... N molecules. There is one integral representing each possible set of interactions, with diagrams representing more molecules being smaller in magnitude than integrals representing more molecules.

$$Z_c = 1 + \text{diagram 1} + \text{diagram 2} + (\text{diagram 3}) + \text{diagram 4} + \text{diagram 5} + \text{diagram 6} + (\text{diagram 7}) + (\text{diagram 8}) + \dots \quad (8.20)$$

From this we can see the largest correction factor is related to only pairwise interactions, therefore if we find a pairwise model of the potential, it can accurately represent the overall potential.

One pairwise model of the potential is known as the Lennard-Jones potential, as described previously, and it includes a large repulsive term, representing the boundaries of the molecules themselves, and a smaller attractive term, that comes from a spontaneously fluctuating dipole moment in one molecule attracting another.

$r_0$  represents the distance between the molecular centers at minimum potential, which is around the diameter of a molecule.  $u_0$  is the maximum depth of the potential well, or how strong these intermolecular forces are.

## Problem

Is there a correction to the ideal gas internal energy ( $U = NkT$ ), when adding in the pairwise interactions of 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?

## Solution

Our solution consisted of programming a complete visualization and mathematical representation of a weakly interacting gas using only the first order correction for its energy. What we found was that, yes, clearly there exists some correction between the traditional Equipartition Theorem energy and the actual energy of gasses in everyday life, however, we found that this correction is almost meaningless in the majority of cases.

First, what is the sign of this correction? Without resorting to the simulation one can infer that if some system begins with initial total energy ( $U_{tot}$ ) and at a later time particles start weakly interacting with a negative potential energy ( $-U_{pot}$ ), then for the total energy to remain the same the kinetic energy of the particles at the later time must go up.

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

This would mean that there is a total positive correction to the kinetic energy which is what relates to the Equipartition Theorem's  $= NkT$ . This is consistent with what we found with the simulation as well. (See later values)

Now for the interesting part, what is the significance of this correction? By limitations imposed on us by computational power, technology, and time we could only accurately simulate in the limit of low temperature/low energy and of  $N$  values around 500-1000. From what we found here is only a correction of about 3% to the kinetic energy. Starting with an initial total energy of around 1000 (♣),  $N$  of 500, and particles spread out enough so that they wouldn't interact with each other, a set of 5 trials was taken at sufficient time to consider the system at equilibrium.

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

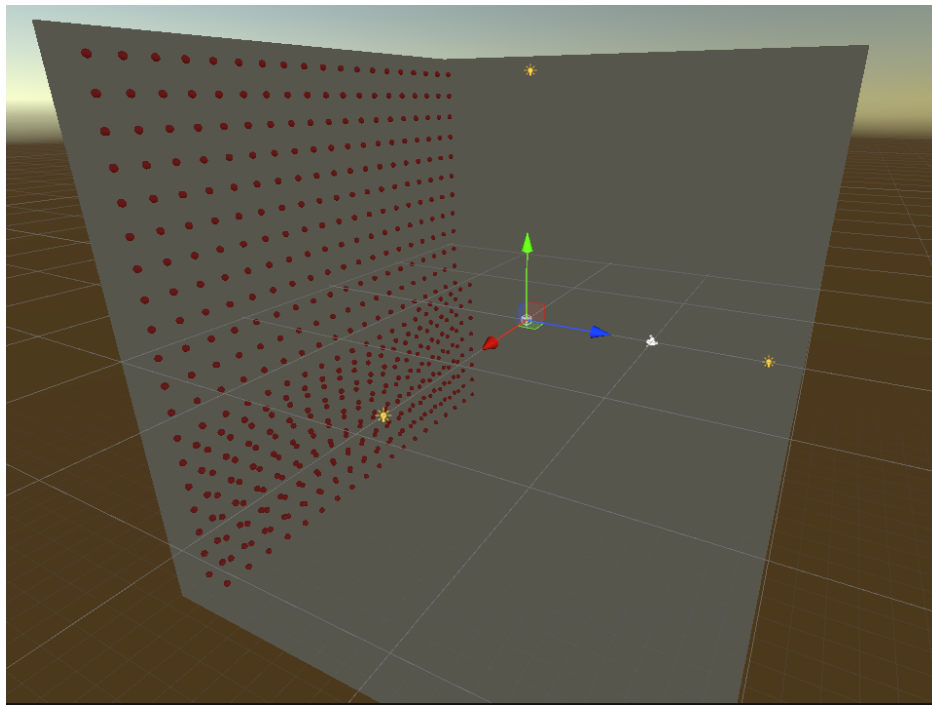
(Note: each of these values are averages over continuous calculations for 2 seconds)

To put this in more tangible terms this is a 3% correction at temperatures around 0.00016K.

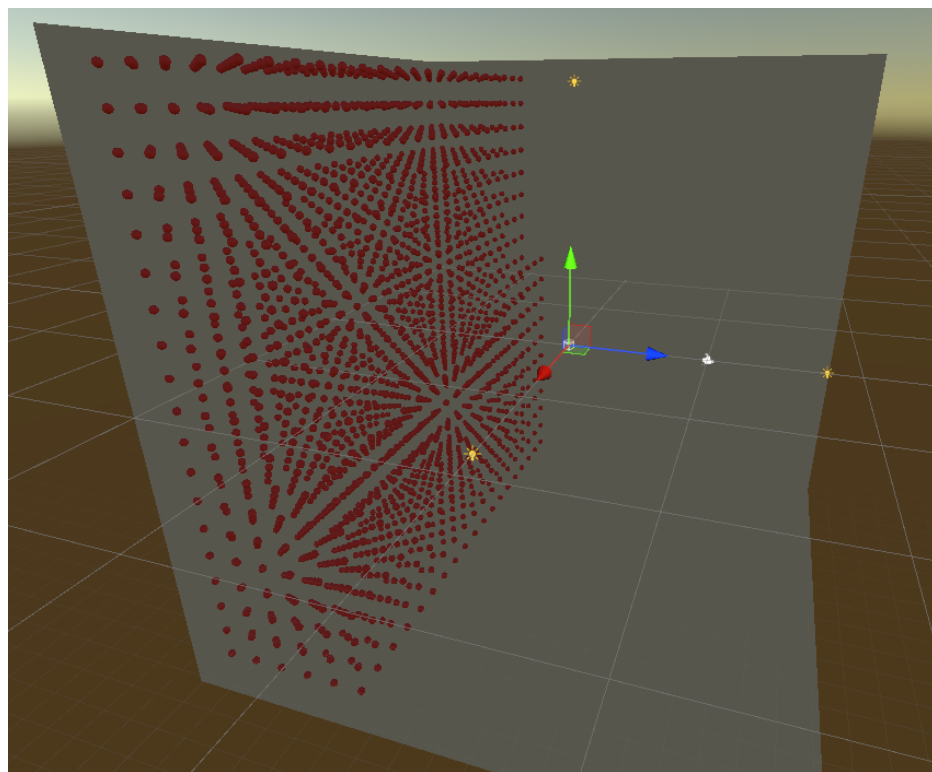
$$T_{initial} = \frac{2(1000)}{3(500)(8263.5)} = 0.00016 K$$

Although, we cannot simulate higher energies as accurately as we can shown here, we still could see trends in the data as we scaled up. What we found was that this correction became much smaller and we can only assume that at energies/temperatures of everyday life this correction will be so small that it is practically non-existent. For example, at initial energy of now 10,000 and N = 500 a data point could give: Total Energy = 9996.227, Potential Energy = -7.836888, and Kinetic Energy of 10004.07; this is a correction of only 0.04%.

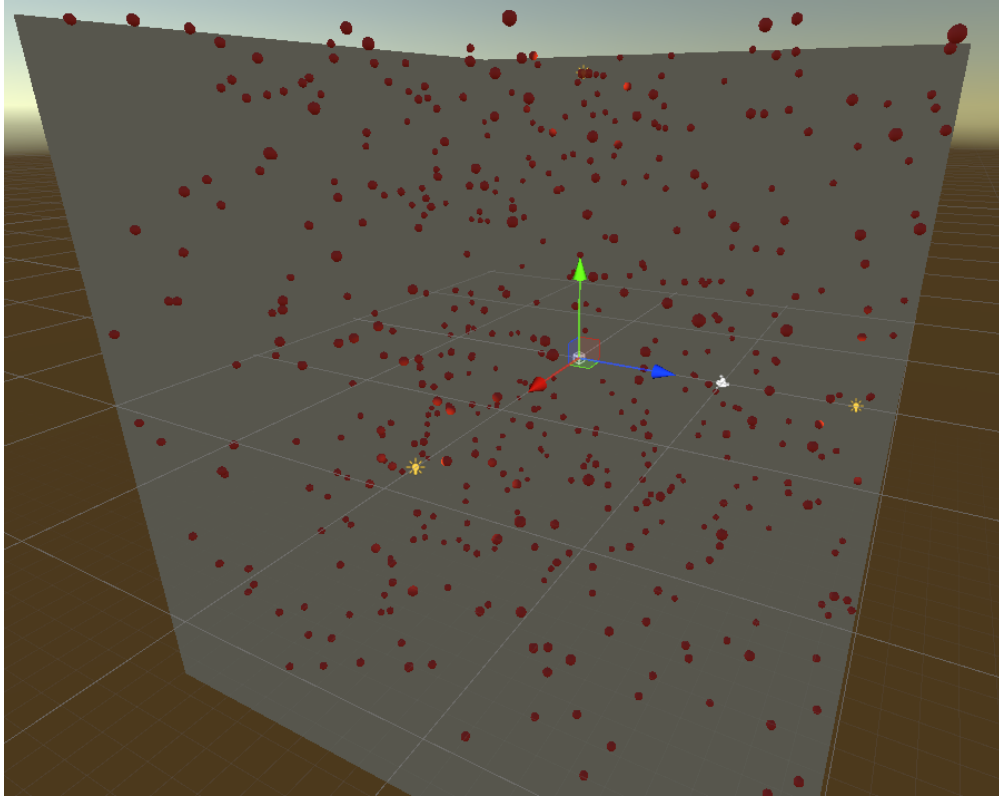
The code can be found [here](#).



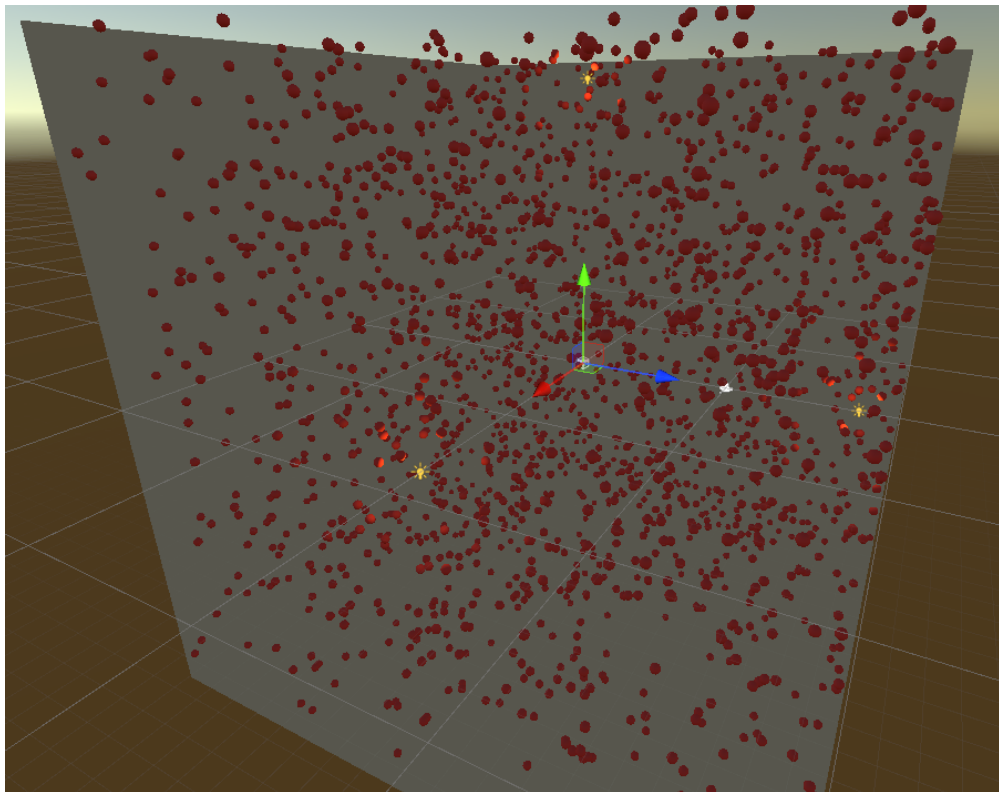
(500 Particles, Initial Configuration)



(2000 Particles, Initial Configuration)



(500 Particles, Final Configuration)



(2000 Particles, Final Configuration)