WRITING AND APPLYING A MONTE CARLO SIMULATION CODE TO EXAMINE AEROSOL VAPOR PRESSURE - AN IMPORTANT FACTOR IN CLIMATE MODELING

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Aerosol nucleation is an important factor in climate change; however, the process of aerosol formation involving atmospheric pollutants is not well understood. The purpose of this study was to examine whether the Kelvin equation (KE) and Classical Nucleation Theory (CNT) can accurately describe the vapor pressure of the nano-droplets involved in aerosol nucleation. A mathematical comparison demonstrates that the vapor pressure of nanodroplets predicted by KE and CNT differ by a factor of $e^{3/2}$. A Metropolis Monte Carlo code was written in Fortran. Monte Carlo simulations in the canonical ensemble for a Lennard-Jones system were used to probe how temperature, total number of atoms, and system size affects the size of a nano-droplet in equilibrium with the surrounding vapor. As expected, varying these three system parameters yields different equilibrium cluster sizes. Somewhat unexpectedly, the simulations indicate that the equilibrium cluster sizes consisting of about 100 to 300 particles are well described by the predictions of both KE and CNT (with linear fits yielding $R^2 > 0.99$). This study is important since experimental measurements are very challenging for small clusters sizes—conditions important for atmospheric nucleation.

Keywords: Aerosol, atmosphere, nucleation, Monte Carlo

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Abbreviations: CNT: Classical Nucleation Theory

INTRODUCTION

Studies have suggested that aerosols are the second most important factor in radiative forcing that impacts climate change; however, the process of aerosol nucleation is not well understood[1,2]. Aerosol nucleation occurs in the atmosphere when gases condense or sublime to form a discontinuous phase of liquid or solid particles (with sizes ranging from nanometer to micron), respectively[1]. These aerosol particles can scatter and adsorb radiation. When water vapor condenses around these aerosol particles, clouds form, which can decrease the amount of sunlight that reaches our planet. A study by Russell suggested that water-vapor condensation around aerosol clusters resulted in a 4% decrease in average worldwide irradiance from the sun in the period from 1960 to 1990[4]. Russell theorized that aerosols lessen global temperatures by deflecting solar radiation; however, a more recent study by Volland suggested that nucleation may also increase global temperatures when black carbon aerosols, such as those formed from combustion of diesel and biofuels, absorb rather than reflect radiation[5] (Figure 1). In fact, a study by Tobin *et al*. suggested that a volcanic eruption filled the atmosphere with aerosols about 200,000 years ago, leading to warming that resulted in a mass extinction on Earth[6]. However, because aerosol nucleation is not well understood, the greatest uncertainty in climate change predictions derives from aerosol formation[1]. The purpose of this

research was to examine the underlying physics of current theories of aerosol nucleation.

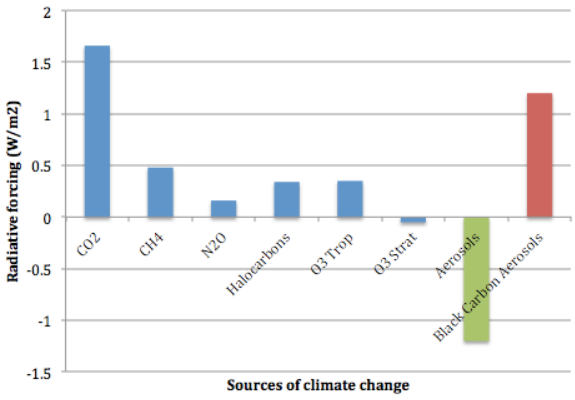

Figure 1. Extent of radiative forcing of sources that contribute to climate change. Positive radiative forcing warms the atmosphere while negative forcing cools it. Aerosols were thought to have an overall cooling effect on the atmosphere, but recent studies have suggested that black carbon aerosols absorb rather than reflect radiation[1,2].

There are a number of theories that attempt to explain the rate of aerosol nucleation and the properties of aerosols. A related question is the equilibrium vapor pressure of nano-clusters in the size-range relevant to atmospheric nucleation. Proposed in the 19th century, the Kelvin equation (KE) (Figure 2) describes the dependence of the vapor pressure increase that results from changing from a planar vapor/liquid or vapor/solid interface to a curved interface of radius *r*. A fault of the KE reported in the literature is that it treats aerosols as macroscopic (using the surface tension and liquid density of the bulk system) when, in fact, they are microscopic[7].

$$\ln\frac{P}{P_0} = \frac{2\sigma v_l}{rRT}$$

Figure 2. KE defines aerosol nucleation, where P is the vapor pressure surrounding the droplet, P_0 is the saturated vapor pressure of the bulk system, σ is the surface tension of the planar interface, v_l is molar volume of the liquid, r is the radius of the droplet, R is the universal gas constant, and T is the absolute temperature[7].

The most prominent theory that attempts to explain nucleation is Classical Nucleation Theory (CNT), which describes free energy of an aerosol cluster (Figure 3). Like the KE, the CNT treats aerosols as macroscopic systems. Studies have shown that CNT can accurately describe aerosol clusters formed from liquid water in equilibrium with water vapor over limited temperature ranges, but not for other aerosol clusters. CNT has been modified to improve accuracy for aerosol clusters other than water, but studies still suggest that the theory is inaccurate[8].

$$\Delta G = N_d^{2/3}\sigma(36\pi)^{1/3}v_l^{2/3} - N_d kT_0 \ln\frac{P}{P_0}$$

Figure 3. The CNT defines the free energy of an aerosol in nucleation, where ΔG is the free energy, N_d is the number of molecules in the cluster, σ is the surface tension of the planar interface, v_l is the molecular volume of the liquid, k is the Boltzmann constant, T_0 is the temperature, P is the vapor pressure of the supersaturated mother phase, and P_0 is the saturated vapor pressure of the bulk system[3].

This study examined aerosol cluster formation in small systems at low temperatures, which are conditions under which aerosol clusters are likely to form in the atmosphere. The specific goals were to:

1. Mathematically compare the Kelvin equation and CNT to determine similarities and differences between the two in order to fully understand both theories;
2. Use Monte Carlo methods to simulate aerosol nucleation in order to determine how numbers of atoms, system size, and temperature affect aerosol clusters formation; and;
3. Compare Monte Carlo simulation results to predictions by the Kelvin equation and CNT to determine accuracy of these theories in examining aerosol nucleation.

MATERIALS AND METHODS

A Unix-based graphics workstation was used with the open-source ifort and gfortran to compile Fortran. Visual Molecular Dynamics software[10] was used to visualize simulation trajectories that were then analyzed using Xmgrace.

Mathematical comparison of the Kelvin equation and CNT: The KE and CNT were mathematically compared by converting variables from CNT into

equivalent variables used in the KE, and making substitutions into the KE.

Monte Carlo simulations: Argon atoms were chosen to make up the nano-droplets in the simulations because their interactions are well understood and simple to model via Lennard-Jones potentials - a mathematical function used to approximate repulsive and attractive interactions between atoms. The two parameters of the Lennard-Jones potential are the well depth and size, and suitable parameters for argon are 0.9977 kJ/mol and 3.400 Å, respectively. The Metropolis Monte Carlo method was used to generate a system trajectory that led to a file of coordinates that represented a fixed number *N* of argon atoms in a three-dimensional cubic simulation box of fixed lengths with periodic boundary conditions. In this study, the number of atoms, the length of the simulation box (*L*), and the temperature (*T*) were varied (Table 1).

An intrinsic function random generator in Fortran 90 was used to randomly assign coordinates to *N* atoms in the simulation box. Next, a single atom was randomly chosen by a random number generator in Fortran, and a Monte Carlo move was attempted to translate the randomly chosen atom to a new location within a radius of 3.4 Å from its original location. The simulations consisted of 30000 *N* cycles of Monte Carlo moves. Clusters were identified using the Stillinger definition of a cluster, where two atoms belong to the same cluster if the distance between them is less than 3.4 Å, and the size of each cluster was calculated. The code was developed to output files containing coordinates recorded every *N* moves and to output the size of the largest cluster in the cube. Simulations were run, first changing the number of atoms, then the simulation box length (i.e., the system volume), and then the temperature using the parameters listed in Table 1. For each condition, 16 or 32 independent simulations were carried out for a total of 208 simulations. Nano-droplet sizes obtained from the simulations were plotted against total number of atoms, simulation box lengths, and temperature.

Microsoft Excel was used to enter data on saturated vapor pressure, surface tension, vapor pressure, and molecular volume of argon at T = 91.5 K (see Table 2) into the KE and CNT to solve for aerosol cluster sizes predicted by these theories through mass balance. Simulation results at T = 90.0 K were plotted with predictions from the KE and CNT, and regression coefficients were calculated to compare simulation results to predictions from the Kelvin equation and CNT. Two-tailed *t*-tests were done to compare significance of changes in cluster size with temperature, with the significance set at $p < 0.05$. Standard deviations for simulation data were calculated from the independent simulations using Excel.

Table 1a. Parameters for simulations examining effects of total number of atoms on cluster size

Test group	Temp (K)	Cube lengths (Å)	Numbers of atoms	Numbers of trials run
1	90	40	75	16
2	90	40	125	32
3	90	40	175	16
4	90	40	225	16
5	90	40	275	16
6	90	40	325	16

Table 1b. Parameters for simulations examining effects of cube length of system on cluster size

Test group	Temp (K)	Cube lengths (Å)	Numbers of atoms	Numbers of trials run
7	90	46	155	16
8	90	48	155	16
9	90	50	155	16
10	90	52	155	16

Table 1c. Parameters for simulations examining effects of temperature on cluster size

Test group	Temp (K)	Cube lengths (Å)	Numbers of atoms	Numbers of trials run
11	45	40	125	32
12	135	40	125	32
2	90	40	125	32

RESULTS

Comparison of the KE and CNT: The KE and CNT depend on the same variables raised to the same powers; however, calculations found in show that the supersaturation ratios (i.e., the enhancement of the equilibrium vapor pressures of nano-droplets

compared to the bulk value) described by the equations differ by a constant factor of $e^{3/2}$.

Table 2. Data from long simulations done to determine the bulk properties of argon at T = 91.2 K, using Lennard-Jones potentials[11]

Temp (K)	Vapor Pressure	Surface tension (N/m)	Vapor density (g/cm^3)	Molecular volume (m^3/molecule)
91.2	125.4072	0.012408	0.006847	4.812×10^{29}

Simulation results: Figures 4 and 5 show representative snapshots taken from a specific Monte Carlo simulation out of 208 simulations runs. Figure 2 shows the initial configuration where T = 90 K, L = 46 Å, and N = 155. Figure 3 shows the nano-droplet at the end of the simulation (after 30,000 N cycles).

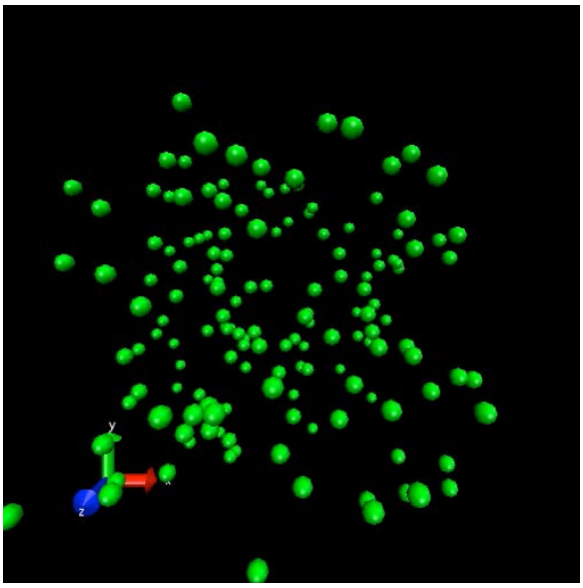

Figure 4. A representative Monte Carlo simulation of 155 argon atoms in a three-dimensional cube of 46 Å lengths at 90 K, where an intrinsic function random generator in Fortran 90 was used to randomly assign coordinates.

Figure 6 shows the average aerosol cluster size plotted against the total number of atoms from 112 simulations of closed systems with T = 90 K and L = 40 Å in comparison to aerosol cluster sizes predicted by the KE and CNT at the same conditions. There is

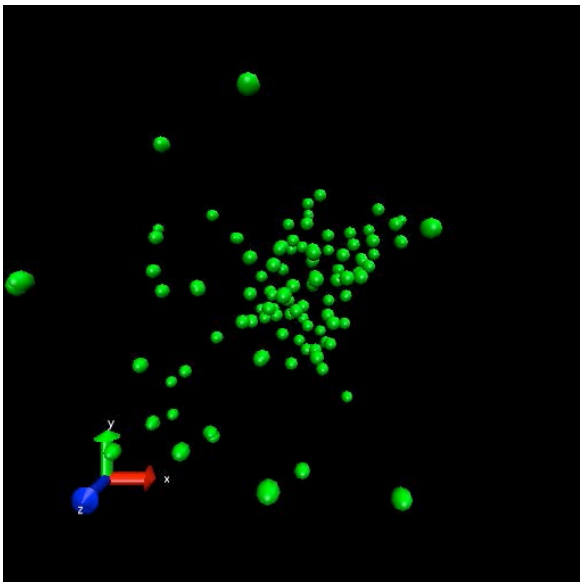

Figure 5. Aerosol formation after the Monte Carlo simulation in Figure 3 was run for 30,000n cycles.

a nearly linear correlation between aerosol cluster size and total number of atoms. The aerosol cluster obtained from the simulations deviates by an average of 2.6 atoms from the KE prediction and by an average of 5.4 atoms from the CNT predictions for system sizes ranging from 125 to 325 total atoms. Simulations were run also for N = 75, stable nano-droplets were not found and neither the KE nor CNT predicted clusters at this condition, so those results are not plotted.

Figure 7 shows average aerosol cluster size plotted against simulation box length from 64 simulations in closed systems containing 155 atoms at T = 90 K plotted with predictions from the KE and CNT at the same conditions. In the simulations, aerosol cluster sizes decreased almost linearly with the inverse volume of the simulations, but the results for the largest box (L = 52 Å) show somewhat more scatter. The simulation data are bracketed by the KE and CNT predictions with average unsigned deviations of 7 and 8 atoms, respectively.

Figure 8 shows average aerosol cluster size plotted against temperature from simulations in closed systems with N = 125 and L = of 40 Å. At T = 45 K, the size of the largest aerosol cluster varied from 52 to 125 atoms, but the lower values come from

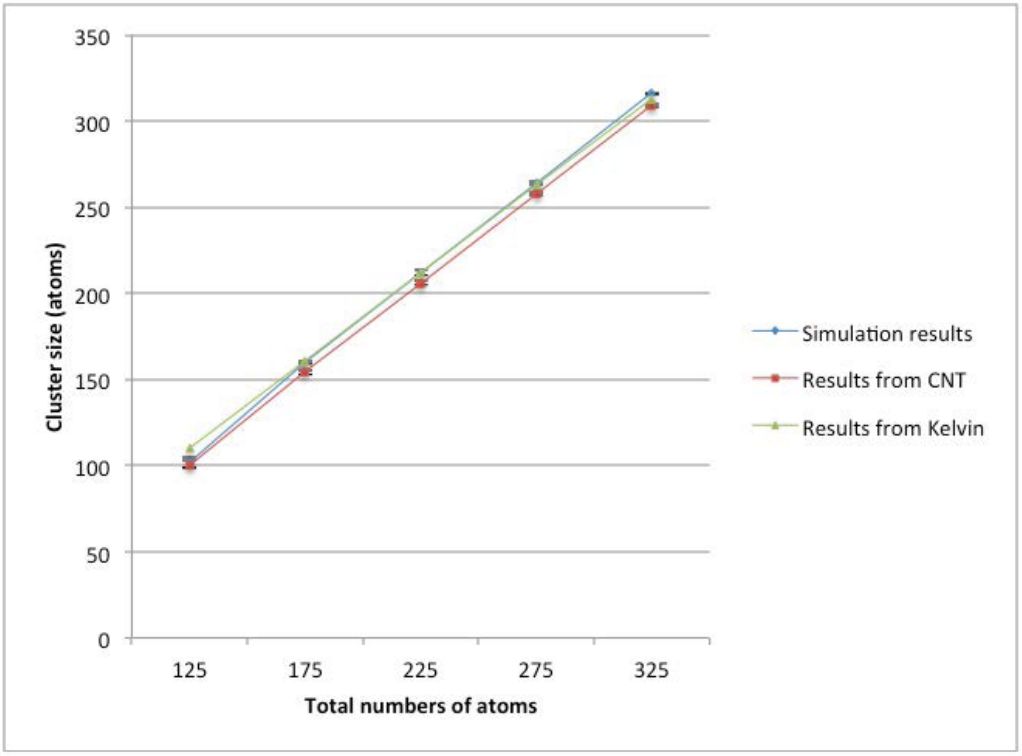

Figure 6. Average aerosol cluster size from 112 simulations of closed systems with cube length of 40 Å and temperature of 90 K gave a direct linear fit with total numbers of atoms for simulations as well for the KEresults and CNT results. Standard error for simulation results is displayed by error bars. (n = 112)

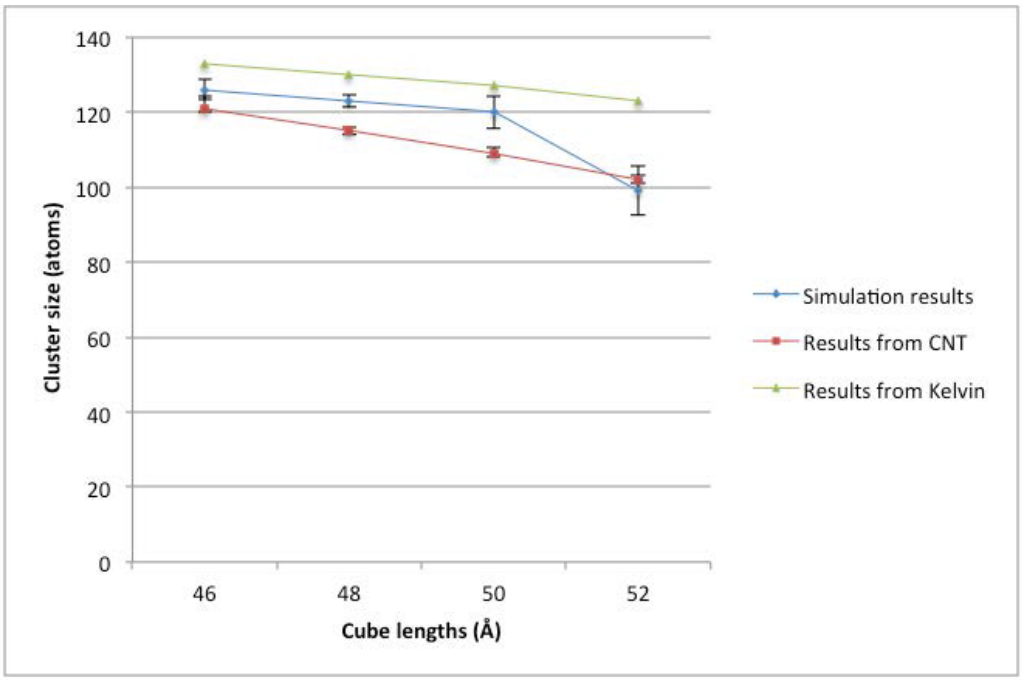

Figure 7. Average aerosol cluster size from 64 simulations in closed systems containing 155 atoms at 90 K decreased in a linear fit with increasing cube length for simulations as well as for the KE and CNT. Standard error for simulation results is displayed by error bars. (n = 64)

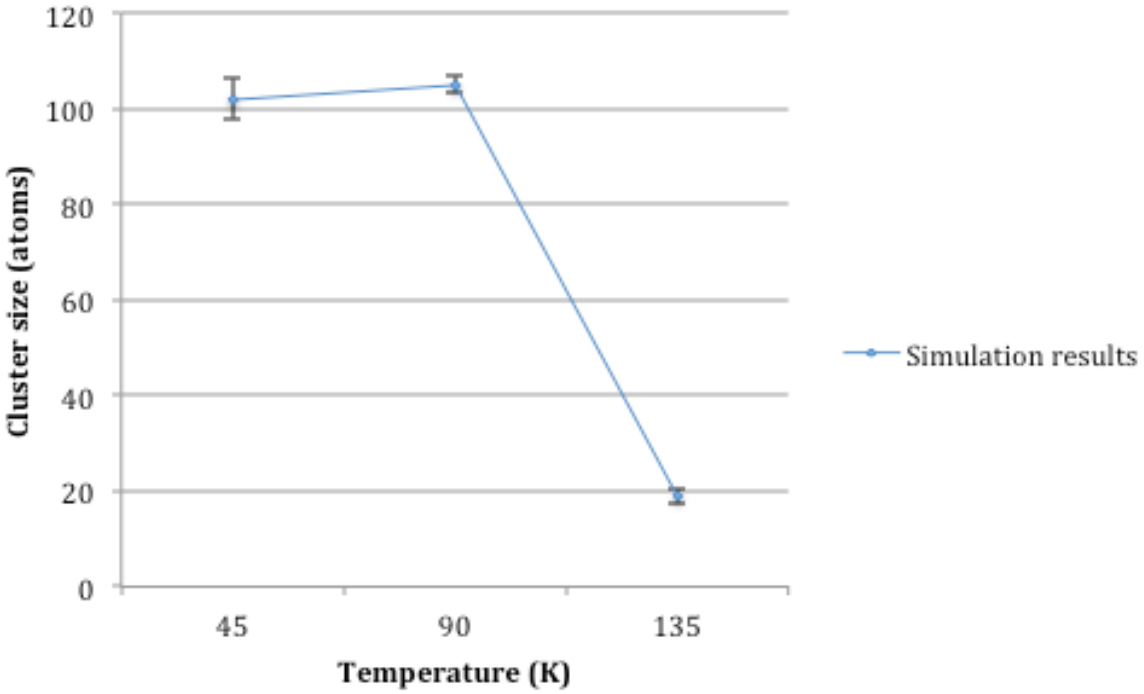

Figure 8. Average aerosol cluster size significantly decreased at 135 K in a closed system containing 125 atoms at cube lengths of 40 Å. A two-tailed *t*-test gave $p = 5.4 \times 10^{30}$, where significance was set at $p = 0.05$. Standard error for simulation results is displayed by error bars. (n = 96)

simulations with multiple cluster being formed that involve all available atoms. The super saturation for this simulation is so high that cluster formation is spontaneous and multiple clusters can form concurrently, and due to the low vapor pressure almost no atoms are found in the vapor region. At T = 90 K, the cluster formation is not spontaneous and only a single cluster is formed with an average size of 105 atoms. A significant drop in cluster size was observed at T = 135 K with an average cluster size of 19 atoms. This drop is caused by the much higher vapor density at the elevated temperature. Representative snapshots of the clusters obtained at these three temperatures are depicted in Figures 9a-c.

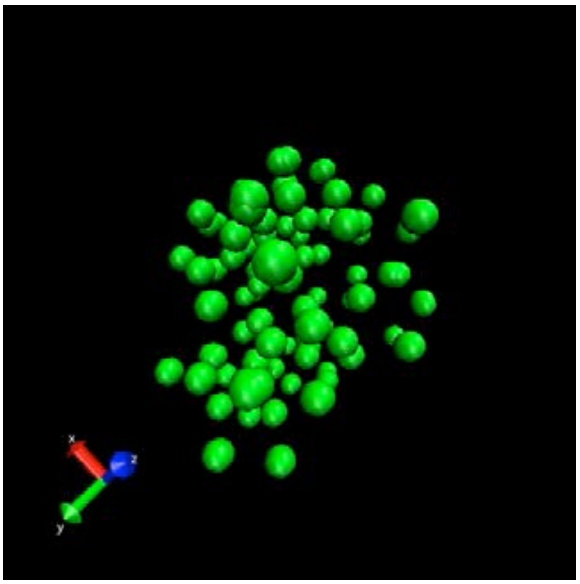

Figure 9a. Final frame of a simulation of 125 atoms with a cube length of 40 Å and a temperature of 45 K.

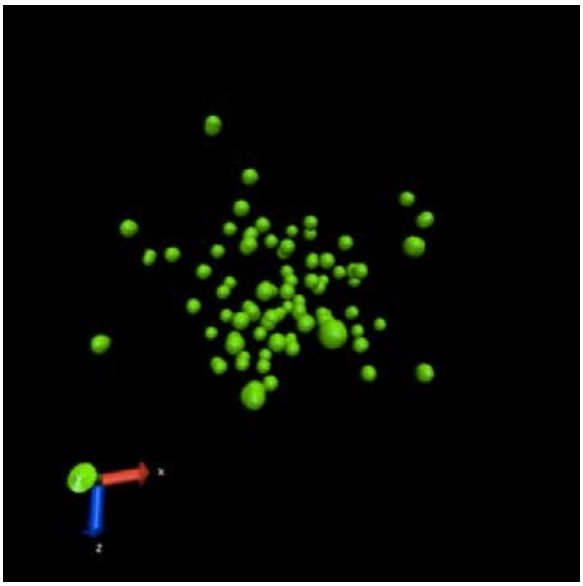

Figure 9b. Final frame of a simulation of 125 atoms with a cube length of 40 Å and a temperature of 90 K.

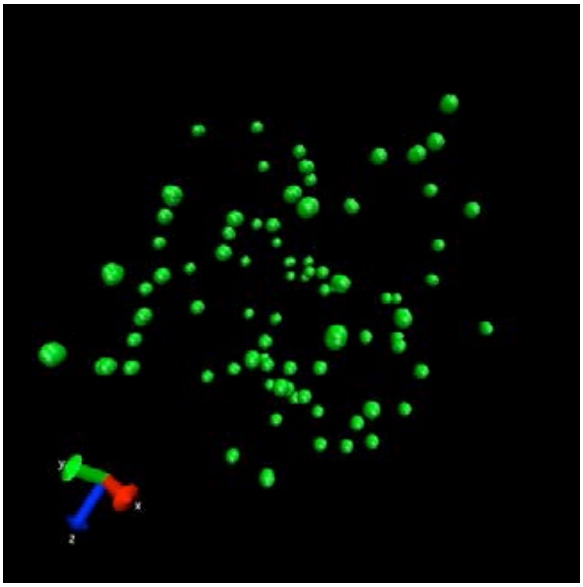

Figure 9c. Final frame of a simulation of 125 atoms with a cube length of 40 Å and a temperature of 135 K.

Figure 10 shows average aerosol cluster sizes obtained from 176 simulations at various overall densities and T = 90 K plotted against average aerosol cluster sizes predicted by KE and CNT at the same conditions. The simulation data agree very well with both theories and correlation coefficients of 0.994 and 0.997 for the KE and CNT, respectively, but this difference is well within the statistical precision of the simulations.

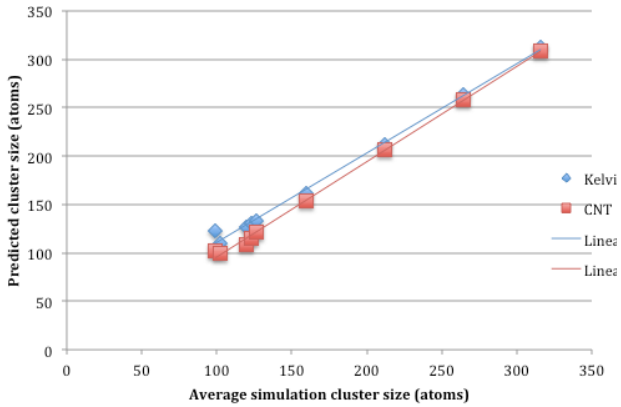

Figure 10. Average simulation aerosol cluster sizes plotted against aerosol cluster sizes predicted by the Kelvin equation and CNT. For the KE, $R^2 = 0.9944$. For CNT, R2 = 0.9976. (n =208)

DISCUSSION

The first goal of the project was to mathematically compare the KE with CNT prediction for the equilibrium vapor pressure of small aerosol particles. This comparison shows that the KE and CNT predictions depend on the same variables raised to the same powers, but the magnitude of the predicted equilibrium cluster size differs by a constant factor of $e^{3/2}$.

The second goal was to write a Monte Carlo simulation code that can be used to examine aerosol nucleation or argon atoms in a small closed system (the canonical ensemble) with different numbers of atoms, system volumes, and temperatures explored as input parameters.

The third goal was to determine the accuracy of the KE and CNT in predicting the equilibrium vapor pressure of nano-droplets. For this assessment, the KE and CNT predictions for the equilibrium vapor pressure and the conditions of mass balance in a closed system are used to calculate the aggregate size predicted by the KE and CNT. Comparisons of simulation results to the KE and CNT predictions for different system densities (i.e., varying either the number of atoms in a constant volume or changing the volume for a constant number of particles) at T = 90 K yield very good agreement. For conditions where the average aerosol size varies from about 100 to 320 atoms, the CNT and KE predictions yield average deviations of about 1% and 2%, respectively, and the correlation coefficients for linear fits of the predictions versus the simulation date are greater than 0.99. Although the CNT was marginally more accurate than the KE, the latter was surprisingly effective.

At low temperature (T = 45 K), simulations showed that nearly all of the available atoms were incorporated into clusters, although sometimes in multiple clusters, because the super saturation was very high; whereas at T = 90 K, only a single nano-droplet formed consistently and the average aggregate sizes (and the number of atoms in the vapor region, i.e., not part of the aggregate) were quite consistent over multiple independent simulations. At T = 135 K, the average aggregate size decreased significantly because the super saturation was much lower compared to simulations with the same number density at T = 90 K. Simulation results for the effects of temperature on aerosol cluster size were not compared with the KE and CNT because high-precision bulk simulation data for argon were not available (and T = 45 K is far below the triple point temperature of argon). Future work should include running simulations at T = 135 K and extrapolating data for T = 45 K from super cooled vapor-liquid equilibria to allow for comparisons to be made. Simulations at lower number density ($L > 52$ Å) were not possible with the current Monte Carlo simulation code because increasing L by even 1 Å increased the processing time of the simulation by a factor of ten. Future work should involve specialized Monte Carlo algorithms tailored to efficiently sample aggregation processes[10].

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