Subcritical and Supercritical Nanodroplet Evaporation: A Molecular Dynamics Investigation

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Abstract
Molecular dynamics simulations are used to investigate the subcritical and supercritical evaporation of a Lennard-Jones (LJ) argon nanodroplet in its own vapor. Using a new technique to control both the ambient temperature and pressure, a range of conditions are considered to define a transition line between subcritical and supercritical evaporation. The evaporation is considered to be supercritical if the surface temperature of the droplet reaches the LJ argon critical temperature during its lifetime. Between ambient temperatures of 300 K and 800 K, the transition from subcritical to supercritical evaporation is observed to occur at an ambient pressure 1.4 times greater than the LJ argon critical pressure. For subcritical conditions, the droplet lifetimes obtained from the simulations are compared to independently predicted lifetimes from the $D^2$ law.

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Introduction

The ability to predict droplet evaporation rates (and thus lifetimes) is important in non-premixed spray combustion applications such as liquid rocket engines, gas turbines, and Diesel engines [1]. The droplet evaporation rate in a subcritical environment with negligible forced or natural convection effects is well described by the $D^2$ law [1]. This model predicts the time rate of change of the square of the droplet diameter, $D$, to be constant, i.e.,

$$\frac{dD^2}{dt} = -K,$$

where $K$ is the evaporation coefficient and $t$ is time. By assuming constant droplet and vapor properties, and a spherical droplet with uniform temperature, $K$ is predicted from the conservation equations to be [1]

$$K = \frac{8\rho V \delta V}{\rho L} \ln \left[ 1 + \frac{c_p V \Delta T}{h_{LV}} \right],$$

where the superscripts $V$ and $L$ indicate the vapor and liquid phases, $c_p$ is the constant pressure specific heat, $\Delta T$ is the difference between the ambient vapor temperature, $T_{\infty}$, and the droplet surface temperature, $T_s$, $\rho$ is density, $\delta$ is the mass diffusion coefficient, and $h_{LV}$ is the latent heat of vaporization.

While the assumptions used in the derivation of $K$ are valid for droplet conditions below the critical temperature, $T_{cr}$, and critical pressure, $P_{cr}$, (i.e., subcritical evaporation), they become questionable for droplets at and near the critical point conditions (i.e., supercritical evaporation) as the surface tension of the droplet approaches zero (reducing the validity of the spherical droplet assumption) and the liquid and vapor phases become indistinguishable ($h_{LV}$ approaches zero). Since many combustion systems operate at temperatures and pressures a factor of two or more times the critical properties of the fuel [2], there is a potential for supercritical evaporation and a need for models that can predict the droplet evaporation behavior for these conditions.

Molecular dynamics (MD) simulations have become a valuable tool in the study of droplet evaporation because no a priori assumptions need to be made about the thermodynamic properties or behavior of the system. Due to computational limitations, the MD method is best suited to studying the evaporation of nanodroplets (i.e., droplets with initial diameters on the order of a few nanometers). In simulations of argon nanodroplets, Kaltz et al. [3] found that droplets with diameters larger than 8 nm have the same $K$ value. Consolini et al. [4] also found that $K$ was independent of droplet size for droplets with initial diameters greater than 3.4 nm, showing the applicability of the predictions of MD simulations to larger droplets.

Previous investigations have used MD to predict the behavior of a nanodroplet evaporating into a surrounding vapor [5, 6, 4, 3]. Long et al. [6] examined the subcritical evaporation of a Lennard-Jones (LJ) argon nanodroplet into its own vapor. They compared their simulation results to predictions obtained through Knudsen aerosol theory, which predicts a constant time rate of change of the droplet diameter. They show the droplet size history from the initial diameter of 3.3 nm to a diameter of 2.4 nm, and over this small range, the droplet diameter history does appear linear, although with the scatter present in their data, it is possible that a fit to a $D^2$-law type history could have also been concluded. Walther et al. [5] also examined the subcritical evaporation of an argon nanodroplet into its own vapor. It was found that the $D^2$ law predictions of $K$ agreed with the simulation results to within 5% to 35% with the accuracy increasing as the initial droplet diameter and potential cutoff radius were increased. Consolini et al. [4] studied the subcritical and supercritical evaporation of xenon nanodroplets in nitrogen environments. It was found for the subcritical case that an initially non-spherical droplet quickly became spherical, while for the supercritical case, the droplet never regained its sphericity due to the lack of surface tension. Kaltz et al. [3] studied the subcritical and supercritical evaporation of liquid oxygen nanodroplets into helium and hydrogen environments. It was determined that pressures much higher than the critical pressure of oxygen were required for supercritical evaporation to occur. The transition point between subcritical and supercritical evaporation was not identified in either of the MD studies that considered supercritical evaporation [4, 3].

The results of additional theoretical and experimental examinations of subcritical and supercritical evaporation have been compiled in review articles by Givler et al. [2], Yang [7], and Bellan [8]. Givler et al. [2], find that numerical and experimental studies of liquid oxygen and paraffin droplets indicate that it is possible for supercritical evaporation to occur when $T_{\infty}$ and $P_{\infty}$ are approximately a factor of two greater than the critical properties. It is also noted that the exact values for the transition are dependent on the droplet and vapor species involved.

In this work, MD simulations are used to determine the transition point between the subcritical and supercritical evaporation of an LJ argon
nanodroplet. In addition, comparisons are made between simulation data for subcritical evaporation and independently predicted lifetimes from the $D^2$ law.

**Molecular Dynamics Simulations**

*Interatomic potential and simulation details*

In an MD simulation, the time history of the positions and velocities of a set of atoms are predicted using the Newtonian equations of motion. In our simulations we model the evaporation of an initially spherical argon nanodroplet in its own vapor. The atomic interactions are modeled using the Lennard-Jones (LJ) 12-6 pair potential, where the potential energy, $\phi_{ij}(r_{ij})$, between two atoms, $i$ and $j$, separated by a distance $r_{ij}$ is given by

$$\phi_{ij}(r_{ij}) = 4\epsilon_{LJ} \left( \frac{\sigma_{LJ}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{LJ}}{r_{ij}} \right)^{6},$$

where $\sigma_{LJ}$ and $\epsilon_{LJ}$ are the zero-energy pair separation distance and potential well depth, $\epsilon_{LJ} = 1.67 \times 10^{-21}$ J, and $\sigma_{LJ} = 3.40 \times 10^{-10}$ m [9]. The mass scale, $m_{LJ}$, is $6.63 \times 10^{-26}$ kg, the mass of one argon atom. The LJ potential has been used extensively in previous investigations of nanoscale thermal transport in solid and fluid phases [10, 11, 12, 13, 14, 15, 16, 17, 18]. Its simple form allows for fast simulations and for the elucidation of phenomena and development of analysis techniques that would not be possible in more complicated systems. A truncated and shifted cutoff scheme is used with a cutoff radius of $2.5\sigma_{LJ}$ and a time step of $0.005\sqrt{\sigma_{LJ}^2 m_{LJ}/\epsilon_{LJ}}$ (10.7 fs). Periodic boundary conditions are imposed in all directions, and the equations of motion are integrated using the velocity Verlet algorithm.

The initial system configuration for all simulations is a spherical droplet at equilibrium with its vapor. The initial configuration was created from the output of separate liquid-only and vapor-only simulations. Both of these simulations contained 1372 atoms, and the system cell length in each case was chosen in order to achieve densities of 1231 kg/m$^3$ for the liquid and 33.7 kg/m$^3$ for the vapor (corresponding to saturation conditions at a temperature of 97 K [19]). The single phase simulations were run in the $NVE$ (constant mass, volume, and energy) ensemble at saturation temperature for 1.07 ns (100,000 time steps). This equilibration period was found to be sufficient to obtain Maxwell-Boltzmann statistics. The droplet was created by cutting the largest possible sphere from the liquid simulation output, and the vapor was created by cutting a spherical hole of the same size from the vapor simulation output. The droplet was then combined with the vapor. At this point, the distance between all droplet and vapor atom pairs was calculated. If any distance was less than $0.9\sigma_{LJ}$ (the start of the first peak in the radial distribution function) either the droplet or vapor atom was randomly deleted so as to prevent the system from starting with any very large forces. The resulting configuration was then run for an additional 1.07 ns (100,000 time steps) in the $NVE$ ensemble. During this period, there was no significant change in the droplet mass, indicating that the droplet was in equilibrium with its vapor. The final configuration, shown in Fig. 1, is a droplet with a diameter of 4.9 nm (710 atoms) in equilibrium with its vapor (1381 atoms) at a temperature of 92 K in a cubic simulation cell with side length, $L$, equal to 13.9 nm (= 40.9$\sigma_{LJ}$).

![Figure 1](image.png)

**Property measurement**

The droplet size is determined at every time step using a modified version of the Amsterdam method described by Sumardiono et al. [20] that is based on counting the number of atoms in the droplet, $N_d$. In this method, atom $i$ is considered to be in the liquid phase if it has at least four nearest neighbors. Atom $j$ is a nearest neighbor to atom $i$ if
the distance between these two atoms is less than 1.5σLJ. Our modification to this method (which assumes that all liquid atoms are also in the droplet) is the additional constraint that in order for atom \(i\) to be considered in the droplet it must be within a distance of \(R_{d,old} + \sigma_{LJ}\) of the last known droplet center (\(R_{d,old}\) is the last known droplet radius). This modification was found to be an effective method of reducing the possibility of liquid atom clusters in the vapor region being classified as part of the droplet. The droplet radius is then determined by finding the minimum distance from the droplet center of mass that contains \(N_d\) atoms.

The liquid and vapor densities and temperatures are calculated for each of \(N_s\) concentric shells centered at the center of the droplet. The inner radius, \(r_{\alpha,i}\), and outer radius, \(r_{\alpha,o}\), of each shell are given by

\[
r_{\alpha,i} = (\alpha - 1) \frac{L}{2N_s},
\]

and

\[
r_{\alpha,o} = \alpha \frac{L}{2N_s},
\]

where \(\alpha\) is the shell label, which ranges from 1 to \(N_s\). We use \(N_s = 20\).

The density of the \(\alpha\)-th shell is found from

\[
\rho_{\alpha} = \frac{3}{4\pi} \frac{\sum_{i \in \alpha} m_i}{(r_{\alpha,o}^3 - r_{\alpha,i}^3)},
\]

where \(m_i\) is the mass of atom \(i\) and the summation is over all atoms in the shell.

In order to calculate the temperature of each shell, two corrections must be made to the atomic velocities. First, the velocity associated with the drift of the system’s center of mass, \(v_{CM}\), must be subtracted from the velocity of each atom. The non-zero \(v_{CM}\) is a consequence of the pressure-control scheme discussed in the next section. The center of mass velocity is calculated as

\[
v_{CM} = \frac{\sum_i m_i v_i}{\sum_i m_i},
\]

where the summation is over all of the atoms in the system.

The second correction is made to account for the radial drift velocity of evaporated atoms as they move away from the droplet, which should not be included in the temperature calculation. Sumardiono et al. [20] outline a procedure that can be used to correctly calculate the temperature of a shell. Their procedure is repeated here in a more general form that allows for multiple-species simulations.

We first calculate the radial component of the velocity of each atom, \(v_{i,r}\), from

\[
v_{i,r} = \left(\frac{v_i - v_{CM}}{|\mathbf{r}_i|}\right) \cdot \mathbf{r}_i,
\]

where \(\mathbf{r}_i\) and \(v_i\) are the position (measured from the center of the droplet) and velocity of atom \(i\). The total drift velocity of the \(\alpha\)-th shell is the sum of all the radial velocities of the atoms in the shell, i.e.,

\[
v_{D,\alpha} = \sum_{i \in \alpha} \frac{m_i v_{i,r}}{|\mathbf{r}_i|}.
\]

The thermal component of \(v_i\) is then

\[
v_{i,t} = v_i - v_{CM} - v_{D,\alpha} \frac{\mathbf{r}_i}{|\mathbf{r}_i|},
\]

and the temperature of the \(\alpha\)-th shell is

\[
T_{\alpha} = \frac{1}{3k_B N_{\alpha}} \sum_{i \in \alpha} m_i |v_{i,t}|^2,
\]

where \(k_B\) is the Boltzmann constant and \(N_{\alpha}\) is the number of atoms in the \(\alpha\)-th shell. We note that the required corrections to the velocities are small, with \(|v_{i,t}|\) typically within 2% of \(|v_i|\).

In subsequent plots, \(\rho_{\alpha}\) and \(T_{\alpha}\) are placed at the radius that is the midpoint of the shell (by volume),

\[
r_{\alpha} = \left[ \frac{(r_{\alpha,i}^3 + r_{\alpha,o}^3)}{2} \right]^{1/3}.
\]

**Ambient pressure and temperature control**

The ambient pressure and temperature are controlled in the “far-field” region. The far-field is defined as the region beyond a radius \(r_{\infty}\) from the center of the droplet. An \(r_{\infty}\) value of 18σLJ was found to be sufficient to eliminate any effects on the evaporation of the droplet and to have enough atoms in the far-field so that the control schemes do not significantly affect the system dynamics.

The far-field temperature, \(T_{\infty}\), is kept constant over the course of the simulation through velocity rescaling. \(T_{\infty}\) is calculated by applying Eqs. (7) to (11) to the atoms in the far-field region. The far-field pressure, \(P_{\infty}\), is controlled by maintaining a constant far-field density, \(\rho_{\infty}\), through the deletion of an atom in the far-field when the density becomes...
too high or the addition of an atom when the density becomes too low. When adding an atom to the far-field region, the randomly chosen location is first checked to see if there are any atoms within 1.12\textit{R}_\text{LJ} [the location of the minimum in Eq. (3)] of the location. This step is done to avoid sudden changes in the forces on the atom. If the location fails this criterion, then a new location is chosen. Adding and deleting atoms over the course of the simulation causes momentum to not be conserved in the system and leads to a required correction to the temperature calculation discussed in the previous section.

The far-field density is allowed to fluctuate between 0.99\textit{\rho}_\infty and 1.01\textit{\rho}_\infty to minimize the effect of the pressure control on the natural system dynamics. The pressure control does not have a noticeable effect on the droplet lifetime, but allows for better control of the ambient conditions (previous studies [6, 4, 5, 3, 20] have allowed the ambient pressure to increase over the course of the simulation as atoms leave the droplet and enter the vapor) and decreases the simulation time (proportional to the square of the total number of atoms).

The critical temperature and pressure of LJ argon are 130 K and 4.1 MPa [19]. To model both subcritical and supercritical conditions, we consider \textit{T}_\infty values between 300 K and 800 K, and \textit{P}_\infty values between 1.05 MPa and 11.65 MPa (corresponding to densities of 16.87 kg/m$^3$ and 109.65 kg/m$^3$). The ambient control techniques are applied at the start of each simulation in order to model the conditions experienced by a cold droplet that is suddenly exposed to a high temperature and high pressure environment.

**Results and Discussion**

**Droplet lifetime**

The droplet lifetime is comprised of two periods: the heating period, \(\tau_h\), where there is no significant change in the droplet mass, and the evaporation period, \(\tau_e\). The sum of \(\tau_h\) and \(\tau_e\) give the total droplet lifetime, \(\tau_d\). These periods are clearly identifiable in the time history of the number of atoms in the droplet shown in Fig. 2 for the \(T_\infty = 600\) K, \(P_\infty = 7.6\) MPa case as an example (note the change in the slope). We define \(\tau_h\) as the time it takes for the mass of the droplet to fall below 97% of its initial value, which we have found to be a good indication that the droplet has begun to evaporate. For the plotted case, \(\tau_h\) is 12 ps and \(\tau_d\) is 58 ps.

The magnitude of \(\tau_h\) is related to the time that it takes for the effects of the far-field region to propagate to the droplet surface at the start of the simulation. This time period is shown in Fig. 3 for the same conditions presented in Fig. 2 by plotting the spatial variation of the temperature at different times. During the time range shown, the vapor region is heating up from its initially uniform temperature of 92 K, and mass is being transferred from the higher density far-field region to the rest of the vapor. The amount of time for this period to occur is approximately \(\tau_h\) (compare with Fig. 2).

**Subcritical to supercritical transition**

We identify the droplet evaporation as being subcritical or supercritical based on the temperature at the droplet surface, \(T_s\). If \(T_s\) becomes greater than or equal to \(T_{cr}\) during the droplet lifetime then the evaporation is supercritical, and if \(T_s\) is less than \(T_{cr}\) then the evaporation is subcritical. To make this calculation the droplet is separated into “core” and “surface” regions such that all of the atoms within \(R_d/2\) of the center of the droplet are considered to be in the droplet core, and the rest are in the surface regions. When calculating \(T_s\), we again apply Eqs. (7) to (11) with the summations now over all atoms between \(R_d/2\) and \(R_d\).

The time histories of \(T_s\) for \(P_\infty = 3.2\) MPa and 8.7 MPa at a temperature \(T_\infty = 600\) K are shown in Fig. 4. The plotted time has been normalized by \(\tau_d\) so that both cases can be compared on the same plot. Each data point in Fig. 4 is an average temperature over 5.36 ps plotted at the midpoint of the interval. This averaging is done to remove fluctuations in \(T_s\) resulting from the finite number of atoms.
Figure 3. Shell temperature (averaged over 2.14 ps intervals) plotted against the distance from the center of the droplet for four different times during the heating period. The droplet surface is at \( r \approx 2.3 \text{ nm} \) during this period, and the far-field region (where the properties are being controlled) is beyond a radius of 6.1 nm. The ambient conditions are the same as those in Fig. 2. The smoothed lines have been included to guide the eye.

in the droplet surface region. For \( P_\infty = 3.2 \text{ MPa} \), \( T_s \) initially increases then remains constant over the rest of the droplet lifetime. Over the entire droplet lifetime \( T_s \) is below \( T_{cr} \) and the evaporation is subcritical. For \( P_\infty = 8.7 \text{ MPa} \), \( T_s \) increases to a value greater than \( T_{cr} \) and the evaporation is supercritical. We note that when \( T_s \) is greater than \( T_{cr} \), the droplet surface is not truly in the liquid state and is instead a high-density vapor. The method used to determine the droplet size (discussed earlier) can still count some of the atoms in this high density vapor as being part of the droplet, allowing \( T_s \) to be greater than \( T_{cr} \). The droplet core temperatures and densities are still below the critical point in these cases and the droplet is still a liquid.

Using \( T_s \) as the indicator of the nature of the evaporation, the results for all of the simulated ambient conditions are shown in Fig. 5 in a plot of ambient pressure scaled by the critical pressure vs. ambient temperature scaled by the critical temperature. Over the range of simulated temperatures, it appears that the transition from subcritical to supercritical evaporation is only dependent on \( P_\infty \). Based on this observation, we plot the droplet \( T_s/T_{cr} \) vs. \( P_\infty/P_{cr} \) (in Fig. 6) for the cases where \( T_s \) is less than \( T_{cr} \) to determine the transition point. For this calculation, \( T_s \) is averaged over the time range from when there are 600 atoms to 50 atoms left in the droplet, corresponding to a time when \( T_s \) is relatively constant. A least-squares regression analysis has been used to fit the data between \( 0.85 < T_s/T_{cr} < 1 \). The resulting fit equation is

\[
\frac{T_s}{T_{cr}} = 0.190 \left( \frac{P_\infty}{P_{cr}} \right) + 0.739, \tag{13}
\]

which gives the transition point where \( T_s = T_{cr} \) to be \( P_\infty/P_{cr} \approx 1.4 \). The value of the transition point is on the same order as the results of previous studies [2, 21], but the independence of \( T_\infty \) for \( T_\infty/T_{cr} \) greater than 2.3 is somewhat surprising. Previous researchers [2, 21] have found that the transition begins to lose the dependence on \( T_\infty \) when \( T_\infty/T_{cr} \) is approximately 3 to 4. The evaporation studied in these works, however, all consisted of droplets evaporating into a vapor of different species.

**Comparison with the \( D^2 \) law**

For subcritical evaporation, \( \tau_e \) can be predicted by integrating Eq. (1) and using the droplet diameter at the start of the \( \tau_e \) region, \( D_e \), as the initial
condition. This gives $\tau_e$ as

$$\tau_e = \frac{D^2}{K},$$

(14)

where $K$ can be determined from Eq. (2). In our calculation of $K$,

1. $\rho^V = \rho_\infty$
2. $\rho^L$ and $h_{LV}$ are evaluated at $T_s$ from the results of Vrabec et al. [19], who used the same cutoff scheme
3. $\rho^V$ is estimated as $2.5R_u$, the constant-pressure specific heat for a monatomic ideal gas (a good assumption at the simulated vapor densities)
4. $\Delta T$ is taken to be the difference between $T_\infty$ and $T_s$
5. $\delta V$ is evaluated at $T = T_s + (1/3)(T_\infty - T_s)$ using separate MD simulations and the Einstein method (see Ref. [22] for details on this approach). We find that $\delta V$ is well correlated by a power-law fit between temperatures of 300 K and 600 K according to $\delta V = (6.65 \times 10^{-9})T^{0.85}$ [m$^2$/s], where $T$ is in K

In Fig. 7, the MD simulation and $D^2$ law predicted values for $\tau_e$ are compared for $\rho_\infty = 33.7$ kg/m$^3$ and $T_\infty$ ranging from 300 K to 700 K. The difference between the predictions increases from 6% at $T_\infty = 300$ K to 37% at $T_\infty = 800$ K. The level of accuracy obtained by the $D^2$ law is similar to what was found in the MD study of Walther et al. [5]. It is believed that the main source of error for the $D^2$-law prediction is due to uncertainty in the specification of $T_s$. Since $\delta V$ and $\rho^L$ are both dependent on $T_s$ ($\rho^L$ is strongly dependent on $T_s$ near the critical point), $K$ is very sensitive to this temperature.

**Summary**

Molecular dynamics simulations have been used to predict the transition between subcritical and supercritical evaporation for an argon droplet evaporating into its own vapor. The ambient pressure and temperature were maintained over the droplet lifetime to allow for better experimental control. The transition was shown to be independent of $T_\infty$ over the range $2.3 \leq T_\infty/T_{cr} \leq 6.2$ and occurs at $P_\infty/P_{cr} \approx 1.4$ (see Figs. 5 and 6). For the subcritical cases with $\rho_\infty = 33.7$ kg/m$^3$, the $D^2$ law was used to predict the droplet lifetimes and comparisons were made with the simulation results. The error of the $D^2$-law prediction was shown to decrease from 37% to 6% as $T_\infty$ decreased (see Fig. 7).

Future work by this group will include: (i) comparing the supercritical evaporation lifetimes with
available models, (ii) expanding the range of simulated ambient conditions to determine if the transition point is always independent of $T_{\infty}$, and (iii) modeling materials with more direct relevance to combustion systems such as hydrocarbons and water.

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**Nomenclature**

- $c_p$: constant pressure specific heat
- $D$: droplet diameter
- $E$: energy
- $h_{LV}$: latent heat of vaporization
- $k_B$: Boltzmann constant
- $K$: evaporation coefficient
- $L$: system cell length
- $m$: mass
- $N$: number of atoms
- $N_d$: number of atoms in droplet
- $N_s$: number of shells
- $r_{ij}$: particle separation
- $r$, $r$: particle position, distance from center of droplet
- $R_d$: droplet radius
- $R_u$: universal gas constant
- $t$: time
- $T$: temperature
- $v$, $v_i$, $v_i$, $v_i$, $v_i$, $v_i$, $v_i$, $v_i$, $v_i$, $v_i$: velocity vector, radial velocity, thermal velocity
- $V$: volume

**Greek**

- $\alpha$: shell label
- $\delta$: mass diffusion coefficient
- $\epsilon_{LJ}$: Lennard-Jones energy scale
- $\phi$: potential energy
- $\rho$: density
- $\sigma_{LJ}$: Lennard-Jones length scale
- $\tau_d$, $\tau_e$, $\tau_h$: droplet lifetime, evaporation period, heating period

**Subscripts**

- $CM$: center of mass
- $cr$: critical point property
- $D$: drift
- $i$: particle label, inner
- $o$: outer
- $\infty$: ambient ("far-field") property

**Superscripts**

- $L$: liquid property
- $V$: vapor property

**References**


