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Evaporative cooling of microscopic water droplets *in vacuo*: Molecular dynamics simulations and kinetic gas theory

Daniel Schlesinger,¹ Jonas A. Sellberg,^{1,a)} Anders Nilsson,^{1,2} and Lars G. M. Pettersson¹

¹Department of Physics, AlbaNova University Center, Stockholm University, SE-106 91 Stockholm, Sweden

²Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA

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In the present study, we investigate the process of evaporative cooling of nanometer-sized droplets in vacuum using molecular dynamics simulations with the TIP4P/2005 water model. The results are compared to the temperature evolution calculated from the Knudsen theory of evaporation which is derived from kinetic gas theory. The calculated and simulation results are found to be in very good agreement for an evaporation coefficient equal to unity. Our results are of interest to experiments utilizing droplet dispensers as well as to cloud micro-physics. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4944387>]

I. INTRODUCTION

The kinetics of water evaporation has been discussed in the literature for a long time and is qualitatively well understood.^{1–3} However, a quantitative, universal description of the evaporation rate has remained a challenge. Within the framework of kinetic theory, evaporation is described by the Boltzmann equation which can be solved using simplifying approximations.⁴ A phenomenological approach consists in the description through the Knudsen theory using an empirical evaporation coefficient α scaling the theoretical maximum evaporation rate to achieve agreement with experimental results. In the literature on water, the value of this evaporation coefficient varies over a wide range.^{5–9}

The generically employed evaporation coefficient α mentioned above is defined as the ratio between the experimental rate, k_{evap}^{exp} , of evaporation and the theoretical maximum value of k_{evap}^{max} , where its value has varied over more than an order of magnitude in former studies of water evaporation.^{5,8} This variation seems to arise mainly from varying accuracies in surface temperature and vapor pressure measurements due to different experimental conditions and apparatuses (see Ref. 5 and references therein). The strong variation of the value of α is not only a problem in experiments: In different molecular simulation studies, completely different values were found. Musolino and Trout, using the finite temperature string method, find a theoretical value of $\alpha = 0.25$ ⁷ while Vieceli *et al.* find a value of $\alpha = 0.99$ using direct molecular dynamics (MD) simulations with a polarizable force field.¹⁰ Varilly and Chandler report a value of $\alpha \approx 1$ from a transition path sampling investigation finding the evaporation process to be consistent with diffusion out of a deep potential well without additional barrier.¹¹ The same authors also emphasize that simulations using

empirical force fields lack quantum effects and thus might not describe the evaporation process sufficiently well in comparison with experiment. However, since apart from the evaporation coefficient α , the Knudsen model depends only on thermodynamic properties, it should be able to describe the temperature of an evaporating droplet with interactions given by a force-field as long as the thermodynamic quantities in the model are those of the force field. This will be the basis of the present study. It should be noted that the evaporation and condensation of water have been studied in MD simulations previously using different force fields,^{10,12–14} while in the present study, the focus is on the description of the evaporative cooling process through the Knudsen theory and the comparison to simulations.

A recent experiment on x-ray probing of water structure upon deep supercooling utilized the principle of evaporative cooling of micrometer-sized droplets in vacuum at rates of $\sim 10^5$ K/s, which allowed measurements at temperatures below the temperature of homogeneous nucleation.^{15,16} Motivated by the experiment, we perform MD simulations of microscopic droplets of TIP4P/2005 water¹⁷ in vacuum to validate the theoretical predictions obtained by the Knudsen theory of evaporation on a 0.1 μ s time scale and length scales of several nanometers. We investigate a droplet size range that clearly shows the limit of the statistical description, where for the smallest droplet size, individual evaporation events show up as temperature jumps in the simulated droplet, and furthermore carefully investigate all possible parameters that determine the evaporation rate.

Our results from straightforward simulations using the TIP4P/2005 water model and the comparison with predictions from the Knudsen theory of evaporation show best agreement for a value $\alpha \approx 1$ for the evaporation coefficient in agreement with Refs. 10 and 11. The results presented are relevant for a basic understanding of evaporation, such as when fuel is injected in a combustion engine¹⁸ or when using evaporative cooling of liquids, particularly water,^{15,16,19} and

^{a)}Present address: Biomedical and X-Ray Physics, Department of Applied Physics, AlbaNova University Center, KTH Royal Institute of Technology, SE-106 91 Stockholm, Sweden.



for the description of atmospheric processes, such as cloud formation.²⁰

II. KINETIC GAS THEORY AND THE KNUDSEN EVAPORATION RATE

The evaporation rate of a substance is commonly calculated from the thermodynamic properties of the liquid using the Knudsen theory of evaporation.^{21,22} The temperature change rate of a volume of liquid subject to evaporative cooling is proportional to the evaporation rate,¹⁻³

$$k_{\text{evap}}(t) = \alpha \frac{P(T)}{\sqrt{2\pi m k_B T}} A(t), \quad (1)$$

and proportional to the temperature change caused by a single evaporation event, thus the temperature change rate of the volume is⁸

$$\frac{dT}{dt} = -k_{\text{evap}}(t) \frac{\Delta H_{\text{vap}}(T)}{\Delta V(t) \rho(T) C_P(T)}, \quad (2)$$

where $T = T(t)$ is the temperature which depends on the interaction time t (i.e., time of evaporation), $P(T)$ is the (surface tension-corrected) saturation vapor pressure, m is the mass of the evaporating molecules, k_B is Boltzmann's constant, $A(t)$ is the time-dependent surface area of the evaporating volume, $\rho(T)$ is the density, $\Delta H_{\text{vap}}(T)$ is the enthalpy of vaporization per molecule, $\Delta V(t)$ is the volume from which evaporation takes place, and $C_P(T)$ is the isobaric specific heat capacity.

Eq. (2) is solved numerically using properties of the simulation model under consideration, but can be used for other models and for real water given that the corresponding temperature-dependent properties are known.

For each time step in the numerical calculation, the heat flux within the droplet is calculated following Ref. 8. The water droplet is modeled as a sphere subdivided into n_{max} spherical shells with a uniform shell thickness of Δr , indexed n , where n decreases with decreasing shell radii, r_n . In Eq. (2), $\Delta V(t)$ and $T(t)$ thus become the volume and temperature of the outermost shell. The heat flow dQ/dt through the surface between the n th and $(n + 1)$ th shell inside a droplet is calculated using Fourier's law of thermal conduction,

$$\frac{dQ}{dt} = -4\pi r_n^2 \kappa \frac{T_{n+1} - T_n}{\Delta r(t)}, \quad (3)$$

where κ is the thermal conductivity, r_n is the radius of the sphere dividing the n th and $(n + 1)$ th shell, and $T_{n+1} - T_n$ is the temperature difference between the n th and the $(n + 1)$ th shell. An energy balance is set up for each spherical shell and the temperature change ΔT_n for the n th shell is then calculated as

$$\Delta T_n = \frac{\Delta Q_n}{M_n C_P}, \quad (4)$$

where ΔQ_n is the net heat flow in/out of the n th shell during a unit step in time and $M_n = \Delta V_n \rho(T)$ is the mass of the n th shell.

Heat conduction is found to be much faster than the energy transport through evaporation for the droplet sizes considered here. The droplets can thus be assumed to cool down in

a quasi-adiabatic manner. The equilibrium thermodynamic properties of the TIP4P/2005 model are used which is justified by the temperature gradient over the droplet being very small at all times (see discussion below).

The pressure inside tiny droplets is increased by the Laplace pressure due to the large curvature of the droplet surface and the surface tension. In the numerical calculations, the saturation vapor pressure is increased due to this effect and is corrected for using the Kelvin equation

$$P(T) = P_0(T) e^{\frac{2\gamma V_m}{rRT}}, \quad (5)$$

with the saturation vapor pressure $P_0(T)$ for a flat interface, the surface tension $\gamma(T, r)$, the molar volume $V_m(T)$, the radius of the droplet r , the gas constant R , and the temperature T . The surface tension is a function of temperature and becomes additionally dependent on the length scales relevant to the interface for very small droplets. Its temperature dependence is described by a modified Guggenheim-Katayama relation,²³ while the length scale correction is determined using the Tolman equation.^{24,25} The exponential correction factor in Eq. (5) for a droplet of $r = 1$ nm, as in a typical MD simulation, evaluates to about 3.1 at $T = 298$ K, while for droplet dimensions of $r = 5$ μm , it is 1.0002 at $T = 298$ K. The correction thus plays a role only on a sub-micrometer length scale and becomes significant only below 10 nm. A lower size limit for the applicability of the Kelvin equation with Tolman-corrected surface tension has recently been shown to lie below 1 nm in MD simulations of the mW model of water.²⁵

Additionally, the effect of mass loss was taken into account. While numerically solving the above set of equations, the evaporation rate was integrated over time providing the total number of evaporated molecules and thus the total mass loss up to the given time step. The radius r of the droplet and the shell thickness Δr were adapted accordingly in every time step.

We obtain an error estimate of the temperature change rate by using propagation of errors of the known uncertainties of TIP4P/2005 model properties. Two different functions for the vapor pressure were used to allow an estimate for the uncertainty: Antoine's law parameterized for TIP4P/2005²⁶ and, alternatively, the Clausius-Clapeyron equation.

III. MOLECULAR DYNAMICS SIMULATIONS

We perform extensive classical molecular dynamics simulations using the empirical rigid TIP4P/2005 model¹⁷ to simulate nanometer-sized droplets *in vacuo* (see Fig. 1) and the evaporative cooling process. We use the program package *GROMACS ver. 4.5.5*.²⁷ Four different droplet sizes were simulated, $r_0 = 1, 2, 3,$ and 4 nm, for up to 100 ns total simulation time. Initially, the droplets contained 141 ($r_0 = 1$ nm), 1120 ($r_0 = 2$ nm), 3767 ($r_0 = 3$ nm), 8985 ($r_0 = 4$ nm) TIP4P/2005 molecules, respectively. The simulations were run at an initial temperature of $T_0 = 380$ K to enhance the number of evaporation events observed per time interval.

Spherical droplets were cut out from a bulk simulation box of TIP4P/2005 water and run in the NVT ensemble for 25 ps to relax surface rearrangements and to achieve

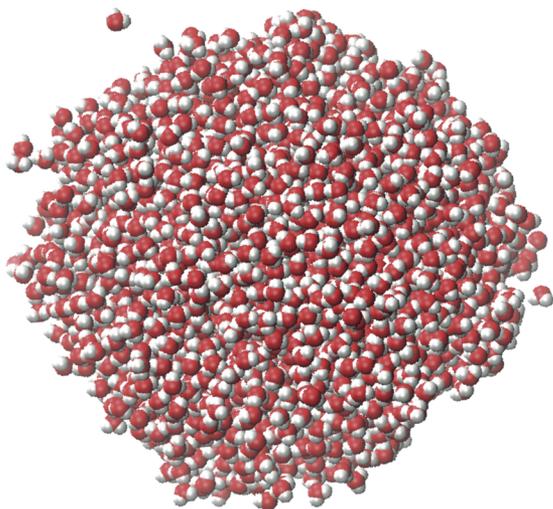


FIG. 1. Typical snapshot of the simulation box with an evaporating droplet in vacuum.

a homogeneous temperature distribution using velocity rescaling. The simulations were then run in the NVE ensemble in double-precision mode; Coulomb and Lennard-Jones interactions were calculated without cutoff. The total energy drift over 100 ns relative to the energy converted from kinetic to potential energy did not exceed 2×10^{-3} . Fluctuations of the time-dependent temperature around a least-squares fit decrease with increasing system size as expected.

IV. RESULTS FROM MD SIMULATIONS AND KINETIC THEORY

In order to assess the performance of the Knudsen theory of evaporation to describe the cooling rate in the simulation,

we compare the simulation results to numerical calculations of the temperature evolution using the theory described above. The temperature-dependent properties (see Fig. 2) entering the theory were obtained from NPT simulations of bulk TIP4P/2005 water for a temperature range of $T = 250\text{--}370$ K in steps of $\Delta T = 10$ K of up to $1 \mu\text{s}$ simulation time with 512 TIP4P/2005 molecules at ambient pressure. The enthalpy of vaporization was calculated as the average potential energy of a bulk phase molecule. The isobaric heat capacity was calculated using the fluctuation formula $C_P = \langle (\delta H)^2 \rangle / (k_B T^2)$ thus obtaining the heat capacity from enthalpy fluctuations. The influence of the Laplace pressure on the computed properties due to the curvature of the nanometer-sized droplets was also considered and found to only affect the vapor pressure. The variation of the factor $\Delta H_{\text{vap}}(T) / (\rho(T) C_P(T))$ with pressure was found to be insignificant for the temperatures and pressures encountered.

Since the surface area, which the evaporation rate is directly proportional to, was found to fluctuate strongly in the simulations, it was computed numerically on a grid every 100 ps along the trajectory and could thus be taken into account for the numerical modeling based on the Knudsen theory of evaporation. The surface was defined as the half bulk-density iso-surface of the density field obtained with the method described in Ref. 28 and then integrated numerically. The area fluctuates over time and the measured area was fitted as a function of time using polynomials of order 5–10 for least-squares fits. The root mean square deviations between the fits and the measured areas were used to estimate the uncertainties and were used in the propagation of errors described above. The relative uncertainties were found to be 1.5% ($r_0 = 4$ nm) and about 4% ($r_0 = 1$ nm).

Fig. 3 shows the temperature evolution in the simulated droplets and the prediction from the Knudsen theory of

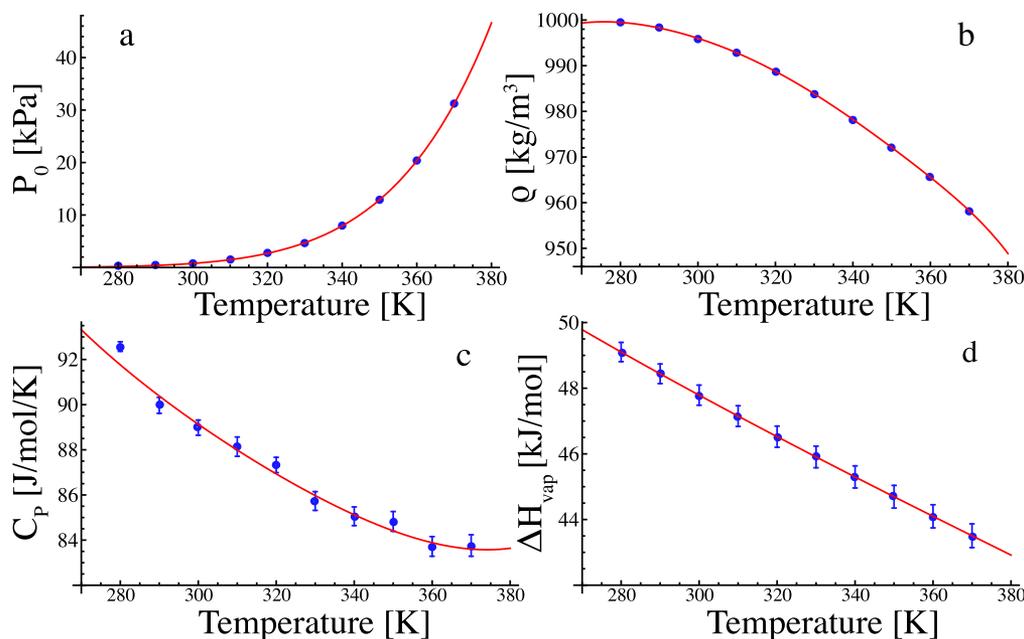


FIG. 2. Temperature dependences of thermodynamic properties of the TIP4P/2005 water model used in the Knudsen theory of evaporation: (a) saturation vapor pressure;²⁶ (b) density; (c) isobaric heat capacity; (d) enthalpy of vaporization. Properties (b)–(d) were calculated from NPT trajectories of up to $1 \mu\text{s}$ simulation time with 512 molecules at ambient pressure.

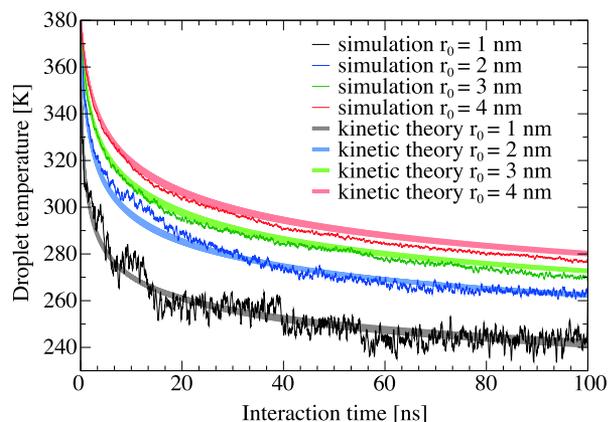


FIG. 3. The temperature evolution due to evaporative cooling in MD simulations of four different droplet sizes ($r_0 = 1, 2, 3,$ and 4 nm) compared to the corresponding results from the Knudsen theory of evaporative cooling. A value of $\alpha = 1$ is used in the Knudsen theory of evaporation. The theoretical results are shown as bands representing the uncertainty interval calculated from the propagation of errors of properties of TIP4P/2005 and the vapor pressure calculated from Antoine's law parameterized for TIP4P/2005²⁶ and, alternatively, the Clausius-Clapeyron equation.

evaporation. The treatment of heat conduction through the droplet with the subdivision into different shells showed that the temperature difference between the inner- and outermost shell is maximally 0.32 K at about 20 ps, while at 100 ns the difference has decreased to 0.0015 K for a droplet of initially $r = 4$ nm. The droplet is thus considered to be close to thermal equilibrium and Fig. 3 shows the mass-averaged temperature over all shells for the Knudsen theory as bands whose width illustrates the uncertainty given by a propagation of errors of the properties of TIP4P/2005 and the vapor pressure calculated from Antoine's law parameterized for TIP4P/2005²⁶ and, alternatively, the Clausius-Clapeyron equation. The temperature decreases very rapidly at high temperatures to then level off at lower temperatures where the evaporation rate decreases drastically. It is only for the smallest droplet size that the temperature is observed to decrease below the melting point of the TIP4P/2005 model of $T_m = 252.1$ K,²⁹ after about 50 ns. A slight underestimation of the cooling rate is visible in Fig. 3 for larger droplets; the temperature in the simulated 4 nm droplet is 3 K lower after 100 ns while that of the 3 nm droplet is 2 K lower than predicted by the Knudsen theory. We note a seemingly improved agreement for the larger droplets compared to the 2 nm droplet although for these small droplets statistical fluctuations in evaporation rate and temperature around the average value are still significant. We conclude that the Knudsen theory of evaporative cooling gives a reliable description of the evaporation and cooling rate of the simulated droplets. Since, apart from the evaporation coefficient, only thermodynamic properties are involved in the Knudsen theoretical model, we expect the model to describe evaporative cooling also for real droplets assuming that realistic thermodynamic functions are supplied. For the micrometer-sized droplets of the experiment in Refs. 15 and 16, we furthermore expect statistical fluctuations to be much smaller and the theoretical Knudsen model to give a reliable prediction of the cooling rate. Indeed, for the smallest

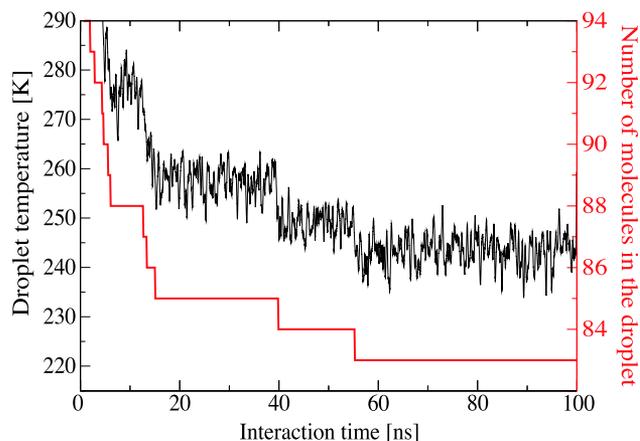


FIG. 4. For the smallest droplet with $r_0 = 1$ nm, individual evaporation events can be identified to cause temperature jumps, while the statistics is poor due to the small number of molecules.

(1 nm) droplet simulated here, individual evaporation events show up as temperature jumps (see Fig. 4), but these are absent already for the 2 nm droplet, which instead shows the expected fluctuations around a mean temperature. The results from the Knudsen theory shown here have been obtained without scaling with α . Since these results seem to slightly underestimate the evaporation rate for the larger droplet sizes, it is clear that scaling with a value below unity would only enhance the discrepancy between theory and simulations. We conclude that the smallness of the deviation between simulation and model does not justify a value of α different from one.

In Fig. 5 we furthermore show the TIP4P/2005 molecules' velocity distribution inside the droplet of initially 4 nm radius within the relatively short time interval of 99.5–100 ns where the droplet temperature is almost constant and the Knudsen theoretical model gives a temperature gradient of 0.0015 K inside the droplet. As expected, this distribution is found to agree well with a Maxwellian velocity distribution for the

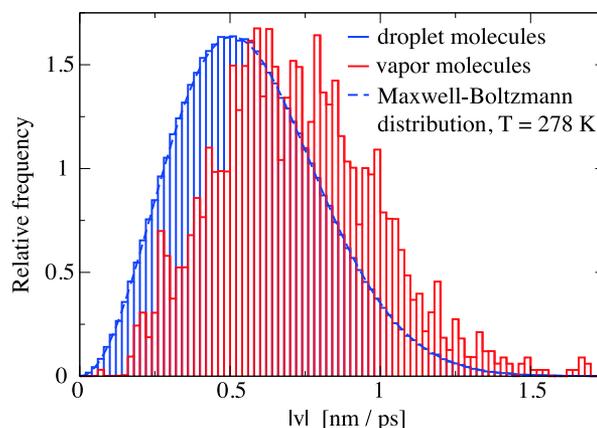


FIG. 5. Normalized velocity distribution of molecules in the liquid phase of a simulated droplet ($r_0 = 4$ nm) collected over the time interval 99.5–100 ns of the evaporation process (blue) which is in good agreement with a Maxwellian at the corresponding average temperature of $T = 278$ K in this interval (blue dashed line). The normalized cumulative velocity distribution of molecules evaporated over the full time interval of 100 ns is also shown (red).

corresponding average droplet temperature of about 278 K in this time interval. As an illustration of the process of evaporative cooling in vacuum, Fig. 5 also shows the cumulative velocity distribution of molecules evaporated over the whole time interval of 100 ns at different droplet temperatures. Since, at each temperature, it is predominantly molecules from the high-energy tail of the distribution that can leave the droplet, it is natural that this histogram of velocities of evaporated molecules is shifted to higher velocities than the mean in the droplet. There is, however, a significant overlap of the cumulative histogram with the less energetic part of the Maxwellian distribution. This reflects the loss of heat of evaporation as the molecules leave the droplet as discussed in Ref. 11 resulting in a downwards shift in energy. We note that the evaporation is into vacuum which means that the molecules that evaporate do not have the possibility to thermally equilibrate due to the extremely low probability of collisions as they move away from the droplet. The form of the velocity distribution after evaporation, but before thermal equilibration in the gas phase, has been given by Varilly and Chandler¹¹ for the case of evaporation at constant temperature. However, the rapidly changing temperature in our droplets and the small number of molecules that evaporate in a given temperature interval result in too poor statistics for a comparison with their result here.

V. CONCLUSION

We use direct MD simulations of nanometer-sized droplets of TIP4P/2005 water to simulate the evaporative cooling process in vacuum. Four different droplet sizes were simulated (1–4 nm initial radius) and run for 100 ns. The simulations were compared to calculations using the Knudsen evaporation rate derived from kinetic gas theory. We use the thermodynamic properties of the TIP4P/2005 model to evaluate the evaporation rate and the temperature change per evaporation event, and find very good agreement between the results from simulations and Knudsen theory. Our results are in best agreement for the evaporation coefficient equal to unity.

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APPENDIX: POLYNOMIAL FITS TO THERMODYNAMIC PROPERTIES OF THE TIP4P/2005 WATER MODEL

$$\begin{aligned}
 C_P(T) &= 746.991\,818\,156\,573 - 7.805\,817\,792\,999\,217 \cdot T + 0.035\,910\,314\,683\,813\,18 \cdot T^2 \\
 &\quad - 0.000\,075\,341\,880\,338\,747\,74 \cdot T^3 + 6.002\,331\,002\,086\,895 \cdot 10^{-8} \cdot T^4 \text{ J/mol K}, \\
 \Delta H_{\text{vap}}(T) &= 140.089\,135\,866\,380\,4 - 1.107\,509\,046\,939\,769\,3 \cdot T \\
 &\quad + 0.006\,067\,148\,412\,500\,480\,5 \cdot T^2 - 0.000\,017\,965\,644\,709\,547\,645 \cdot T^3 \\
 &\quad + 2.701\,443\,164\,501\,017 \cdot 10^{-8} \cdot T^4 - 1.639\,328\,808\,335\,716\,7 \cdot 10^{-11} \cdot T^5 \text{ kJ/mol}, \\
 \rho(T) &= 199\,154.460\,171\,415\,5 - 4798.075\,641\,847\,879\,5 \cdot T + 49.290\,214\,743\,319\,67 \cdot T^2 \\
 &\quad - 0.278\,942\,753\,751\,192\,2 \cdot T^3 + 0.000\,940\,307\,948\,317\,107 \cdot T^4 \\
 &\quad - 1.889\,652\,475\,227\,357\,4 \cdot 10^{-6} \cdot T^5 + 2.097\,335\,403\,903\,993 \cdot 10^{-9} \cdot T^6 \\
 &\quad - 9.922\,135\,928\,718\,443 \cdot 10^{-13} \cdot T^7 \text{ kg/m}^3.
 \end{aligned}$$

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