Critical Nanopore Diameter for Evaporation is 4 nm

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Graphical TOC Entry

Abstract

Evaporation studies of water using classical molecular dynamics simulations are largely limited due to their high computational expense. This study addresses this issue by using a coarse-grained molecular dynamics model for evaporation of water on solid surfaces by combining four water molecules into a single bead. The Morse-D water model which accurately predicts the water properties at higher temperatures is used to study the evaporation from hydrophilic nanopores. The simulation results show that 4 nm is the critical diameter to initiate continuous evaporation at nanopores.

Keywords: Nanopore evaporation, high heat flux, liquid cooling, Morse potential, SPEA

Introduction

The energy consumption has significantly increased over the past decade due to the increasing number of supercomputers and data center-based cloud computing. This trend will continue for decades which will put a strain in the energy sector. This trend also necessitates compact designs with higher energy density and hence calls for highly efficient and faster cooling systems. The cooling system of a data center typically consumes around 40% of the energy input. This projection forecasts to approximately $150 billion per year cost by the year 2030 ¹ and hence research efforts targeting the development of efficient cooling systems is vital in the fields of heat transfer and semiconductors. Among the conventional cooling techniques, evaporative water cooling emanates as a promising candidate due to its high specific heat capacity and high enthalpy of vaporization. Based on kinetic theory, ² an evaporative heat flux of 20,000 W/cm² can be achieved using water at 1 atm.

Past two decades have seen a plethora of research activities in utilizing nanoscale surface structures to enhance the heat transfer from a solid surface to liquid ³-⁷. The studies ranged from theoretical modeling of nanopore evaporation using continuum methods ⁴,⁵ for \( d = 10-100 \) nm, to experimental studies of nanopore evaporation ³,⁵ for \( d = 24-100 \) nm, suggesting that high heat fluxes are possible through nano porous evaporation. But these enhancements are frequently limited by the critical heat flux (CHF) ⁸, contamination ⁴ or due to lack of continuous evaporation at nanopores and structures called dry out conditions. The evaporation characteristics of nanopores with \( d < 10 \) nm is not studied through simulations or via experiments. While the experimental techniques pose challenges to validate and characterize evaporation at this scale, computational tools such as molecular dynamics ⁹-¹¹ can provide promising results without the need for expensive device fabrication and instrumentation. One challenge however is that there is no water model that can capture or simulate all of its properties simultaneously ¹². Even the best performing and widely used models such as SPCE ¹³ and TIP3P ¹² are unsuitable to study water evaporation, due to the excessive...
computational cost (refer supplementary material). This shifts our focus to computationally faster and efficient models, namely coarse grain molecular dynamics (CGMD) models.

In a typical CGMD model, one or more water molecules are combined into a bead or a super-molecule to represent the bulk properties of the system. The field of coarse graining is a large research area and hence the readers are advised to refer to consolidated reviews found elsewhere in the literature \(^{14-16}\). Among various types of CGMD models, mono-bead models are appealing due to their low computational power consumption \(^{17-19}\). Specifically, the generalized Mie potential based water model \(^{19}\), which maps one water molecule to a single bead, can accurately represent density, surface tension, and enthalpy of vaporization of water for a wide range of temperatures. As a special case of Mie potential, Lennard-Jones (LJ) potential is used to map four water molecules to a bead in the classical MARTINI model \(^{17,18}\) which computationally efficient than the former. Most of these existing CGMD models are developed for biomolecular studies \(^{17,20,21}\) and have not been tested for heat transfer studies. The existing CGMD models \(^{21,22}\) mainly focus on the room temperature behavior of water or even sometimes the behavior below zero degrees Celsius. While these models can capture freezing, ice formation and other properties of water \(^{23}\), their applicability to high temperature problems is limited or seldom.

Simulating water heat transfer or evaporation using the MARTINI model in its original form will produce incorrect results; thus, it must be re-parameterized to temperatures near 100 °C, which is closer to the working temperatures of a semiconductor. There exists a few CGMD models developed for the high temperature water evaporation studies \(^{24,25}\). Among them, the MARTINI-E model was optimized using a hybrid ANN-GA-NM (Artificial Neural Network, Genetic Algorithm and Nelder Mead) approach. In a separate study \(^{26}\) the popular potential functions like LJ, Morse, Mie and Stillinger-Weber (SW) are investigated for its suitability for a CGMD water model and found that Morse based potential \(^{25}\) and machine learned SW (ML-mW) potential \(^{23}\) shown good agreement with experimental values. ML-mW has an upper hand on Morse potential when it comes to accuracy and computational speed. However, the latter has good stability and less energy fluctuations with larger time steps of integration. Moreover, ML-mW is 1:1 mapping of water molecules to bead whereas Morse based, and MARTINI models are 4:1 mapping, which ultimately makes them much faster than ML-mW. Hence the studies in this paper are mainly based on the optimization of the water models based on Morse potential and its application on evaporation of water.

The existing Morse potential based water coarse grained model \(^{25}\) is re-parameterized to match the experimental density, enthalpy of vaporization and surface tension at room temperature (20°C aka 293 K as per NIST standards). The optimization process starts with the Nelder-Mead method, followed by the Strength Pareto Evolutionary Algorithm. The optimized model is then compared with the existing CGMD models and the best model suitable for evaporation studies is justified. Using the best model (Morse-D) for evaporation, nanopore evaporation studies are performed and the heat flux is estimated for various nanopore sizes.

**Coarse Grained Models of Water**

The most used coarse-grained model for water is MARTINI (see supplementary material). Other interesting CGMD models of water include machine learned Stillinger-Weber (ML-mW) model \(^{23}\) and extended MARTINI model (MARTINI-E \(^{24}\)) (see supplementary material).

**Morse Potential**

The Morse potential is a convenient inter-atomic interaction model for a diatomic molecule. It provides a better approximation for the vibrational structure of the molecule than the quantum harmonic oscillator \(^{26}\) because it explicitly includes the effects of bond breaking, such as the existence of unbound states \(^{27}\). Though it was originally developed for diatomic molecules, the Morse potential can also be used to model other interactions such as the interaction between an atom and a surface, and recently for CGMD models. The Morse potential energy function takes the form as shown in Eqn. 1

\[
\phi = D_0 \left[ e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)} \right]
\]

\[E = \phi(r) - \phi(r_{cut}) - (r - r_{cut}) \frac{d\phi}{dr} \bigg|_{r=r_{cut}} \]  \hspace{1cm} (2)

Here \(r\) is the distance between the atoms, \(r_0\) is the equilibrium distance, \(D_0\) is the potential well depth, and \(\alpha\) controls the spread of the potential function. For numerical simulations, often a shift and a linear term is added to the potential so that the potential energy and force both attain a value of zero at the cut-off radius (Eqn. 2). Generally, a cutoff radius (\(r_{cut}\)) is used to speed up the calculation using a computer, so that atom pairs with distances greater than the
cutoff radius have an interaction energy of zero or negligible. The advantage of using Morse over the standard LJ potential is due to its versatile tunability using 3 parameters instead of 2. This will avoid sharp jumps in energy wells and can appropriately model the liquid properties near freezing point.

**Molecular System for CGMD simulation**

A lamellar system consisting of liquid film suspended between vapor layers is an ideal candidate to estimate the liquid density, vapor density, surface tension, enthalpy of liquid phase and enthalpy of vapor phase simultaneously. Such a system is constructed as shown in the Fig. 1. Initially, 4.5 nm cubic periodic boundary system with MARTINI beads equivalent to 1,000 kg/m³ was equilibrated under 1 atm pressure and a temperature of 300 K using a Nose-Hoover thermostat and barostat. After equilibrating for 100,000 steps using a time integration step of 20 fs, the z-axis dimension is increased to 18 nm and sides are increased to 4.6 nm. This will form a lamellar system with periodic boundaries and consisting of 864 CGMD beads (equivalent to 3456 water molecules) as shown in the Fig. 1 and is then equilibrated for another 200,000 steps by removing the barostat and using only a Nose-Hoover thermostat at 300 K.

![Figure 1: Lamellar CGMD system used to test the CGMD models.](image)

To estimate the thermodynamic properties from a simulation, the lamellar system is divided into imaginary slabs of thickness $dz = 0.1 \text{ nm}$ as shown in the Fig. 1. The number density, density, enthalpy, and surface tension are then estimated through the following equations.

The density profile is given by,

$$\rho(z) = m_{\text{bead}} N(z)$$  \hspace{1cm} (3)

Here, the $m_{\text{bead}} = 72.0612\frac{g}{\text{mol}}$ is the CGMD bead mass and $N(z)$ is the number density in the $z^{th}$ slab. The enthalpy profile is given by,

$$H(z) = \langle KE(z) \rangle + \langle PE(z) \rangle + \langle P(z)V_{\text{slab}} \rangle$$  \hspace{1cm} (4)

Here, $H$ is the enthalpy, $KE$ is the kinetic energy, $PE$ is the potential energy, $P$ is the total pressure, and $V_{\text{slab}}$ is the volume of the slabs. The surface tension is given by,

$$\gamma = \sum_{z=0}^{L_z} dz \left[ (P_N(z)) - \langle P_T(z) \rangle \right]$$  \hspace{1cm} (5)

Here, $L_z$ is the length of the lamellar system, $P_N$ and $P_T$ are the normal and tangential components of the pressure tensor at $z^{th}$ slab.
Stage-1 Optimization using Nelder-Mead Method

One of the crucial steps in optimizing a potential or force field is the selection of initial bounds or the starting point for the parameters \((D_0, \alpha, r_0)\). For this study, the initial point was obtained from the multi temperature optimized model Morse-D \(^\text{23}\) through a downhill simplex method called Nelder-Mead. This way, the simulation instabilities due to wide density fluctuations can be minimized. The density, surface tension and enthalpy of vaporization of water is estimated from the CGMD simulations and compared with the experimental results through a cost function (average percent error) as shown in the equation 6. Here, \(\delta\) is the average percent error; \(\rho, H, \gamma\) are the density, enthalpy of vaporization and surface tension values from CGMD simulations. The quantities with a subscript of EXP indicate the values from the experiments obtained from the NIST database \(^\text{28}\).

\[
\delta_{\text{cost}} = \frac{100}{3} \left[ \left( \frac{\rho - \rho_{\text{EXP}}}{\rho_{\text{EXP}}} \right) + \left( \frac{H - H_{\text{EXP}}}{H_{\text{EXP}}} \right) + \left( \frac{\gamma - \gamma_{\text{EXP}}}{\gamma_{\text{EXP}}} \right) \right]
\]  

(6)

The Nelder–Mead (NM) method is a commonly applied numerical method \(^\text{29,30}\) to compute the minimum or maximum of an objective (cost) function in a multidimensional space. It is a direct search method and is often applied to nonlinear optimization problems for which derivatives may not be known. The method uses the concept of a simplex, which is a special polytope of \(n + 1\) vertices in \(n\) dimensions. The major steps of this algorithm are sorting the simplex based on the objective function values, reflection, expansion, contraction and shrinking. The simplex is iteratively progressed through multiple dimensions in direct search of the optimum parameters and terminated when the standard deviation of the simplex reached a threshold or upon reaching certain number of iterations. There exist many variations for the numerical implementation of the NM method, of which the current work uses the original method \(^\text{29}\). The algorithm of NM implementation is shown in Fig. 2b. Using this implementation, the Morse parameters are optimized to achieve the experimental values at 293 K (Fig. 2a).

![Figure 2](image-url)

**Figure 2:** a) Phase equilibrium points used to optimize the Morse-D (in red color) and Morse-E (in green color) models of water. b) Flow chart of the Nelder-Mead optimization method implementation.

The cost function (Eqn. 6) chosen for optimization tends to reduce the average error across three thermodynamic parameters. This causes a convergence issue beyond a certain threshold. The results of the convergence are shown in the Fig. 3a. The inset figure shows the zoomed in error value region near 500\(^{th}\) iteration. Apparently, the NM algorithm converged into a local minimum with an error value of 4.2% with \(D_0 = 2.20926, \alpha = 0.59846, r_0 = 5.998474\).
Stage-2 Optimization using Strength Pareto Evolutionary Algorithm

Both NSGA and SPEA are best in solving multi objective optimization problems according to the literature. The latter is easier to implement due to its simplicity. This work used a python code implementation of the SPEA2 \(^{32}\) an upgraded version of the original. Both these methods fall under the \(A \text{ posteriori}\) methods of multi objective optimization techniques, which aims at producing all the Pareto optimal solutions. A detailed explanation of the steps and implementation details of this method is beyond the scope and focus of this work and hence readers are advised to refer the original paper \(^{32}\).

The in-house developed python code is tested and validated for the standard functions for multi objective optimization (see supplementary material). This code is further extended to run the CGMD simulations and estimating the errors. The SPEA2 was started with a population size of 30, archive population of 20, mutation probability of 0.1, and the bounds of the variables were \([1.5, 2.5]\) for \(D_0\), \([0.5, 1.0]\) for \(\alpha\), and \([5.0, 7.5]\) for \(r_0\) respectively. All simulation runs are performed using a time step of integration of 20 \(fs\), for 50,000 equilibration steps followed by 100,000 production steps using a Nose-Hoover (NVT) thermostat using LAMMPS software unless otherwise specified. We call this model as Morse-E which represents the optimization at room temperature. The optimized pareto front after 130 generations is shown in the Fig. 3b. The axes correspond to the percent error for each thermodynamic variable and the color intensity represents the average percent error. After 130 generations of SPEA2, there was no significant improvement in error and found to 0.4 % with the parameters given in the Table 1. For comparison, the other Morse based model parameters are also listed in the Table 1. The Morse-D represents the best optimized model based on three temperatures from my previous study \(^{25}\) and Morse-W4 represents the first study \(^{33}\) using Morse potential for water CGMD model. Note that the time step of integration and cutoff radius used for these models are different. For Morse-D and Morse-E, the cutoff is kept at 1.2 nm for faster performance and \(dt\) as 20 fs for low density and pressure fluctuations during the simulations.

**Table 1**: Optimized parameters of Morse CGMD models

| CGMD Model       | \(D_0\) (kcal/mol) | \(\alpha\) (Å) | \(r_0\) (Å) | \(r_{cut}\) (nm) | \(dt\) (fs) |
|------------------|--------------------|----------------|-------------|------------------|-------------|
| Morse-D \(^{25}\) | 1.686345           | 0.625349       | 5.8106      | 1.2              | 30          |
| Morse-W4 \(^{33}\)| 0.81262            | 0.7            | 6.29        | 1.6              | 40          |
| Morse-E (This work) | 1.850222         | 0.683513       | 5.78284     | 1.2              | 20          |
The Morse-W4 model is aimed at representing the experimental density, enthalpy of vaporization, and surface tension at 298K. However, a larger cutoff radius of 1.6 nm was required for Morse-W4 for accurately represent the properties.

In the next set of studies, CGMD models are compared using cutoff radius of 1.2 nm, time step of 20 fs and using the same lamellar molecular system. The system is equilibrated for 50,000 steps, followed by 100,000 production steps and the temperature is controlled using a Nose-Hoover thermostat. Four different CGMD models of water (MARTINI, Morse-D, Morse-E and Morse-W4) are compared using the same simulation conditions. The temperature of the system is varied from 280 K to 500 K and properties are estimated. To account for the statistical fluctuations, 25 simulations are performed at every temperature with different starting conditions (random momentum of beads) and average quantities are estimated. These average quantities for density, enthalpy and surface tension are normalized with the experimental values are plotted in the Fig. 4a, 4b and 4c respectively.

Figure 4: The ratio between the CGMD simulations and experimental values are shown for a) density, b) enthalpy of vaporization, and c) surface tension. The quantities are estimated for temperatures varying from 280 K to 500 K. The markers indicate MARTINI model (square), Morse-D (triangle), Morse-E (diamond) and Morse-W4 (circle) models respectively.

From the results shown in Fig. 4a, all models except Morse-W4 accurately represent density of water. The Fig. 4b shows the Morse-D perform better among all for enthalpy of vaporization. The surface tension results in Fig. 4c shows Morse-D as a better CGMD model among the selected four models. The superior performance of Morse potential based models for water with very short cutoff radius is promising to study thin film evaporation and wettability studies at nanoscale for temperatures around the boiling point of water.

Table 2: Comparison of various models of water

| Model            | \(\rho_{\text{liquid}}\) (298K) g/cm\(^3\) | \(dH_{\text{vap}}\) (298K) kcal/mol | \(\gamma_{\text{LV}}\) (300K) mN/m | \(T_{\text{MD}}\) (K) | \(\rho_{\text{liquid,max}}\) (TMD) g/cm\(^3\) |
|------------------|------------------------------------------|-----------------------------------|------------------------------------|------------------------|------------------------------------------|
| Exp \(^36\)      | 0.997                                    | 10.52                             | 71.6                               | 277                    | 0.9999                                   |
| mW \(^37\)       | 0.997                                    | 10.65                             | 66                                 | 250                    | 1.003                                    |
| SPCE \(^13\)     | 0.999                                    | 10.76                             | 61.3                               | 241                    | 1.012                                    |
| TIP3P \(^12\)    | 0.986                                    | 10.17                             | 49.5                               | 182                    | 1.038                                    |
| Morse-W4 \(^33\) | 0.998                                    | 9.17                              | 71                                 | 50                     | 0.941                                    |
| MARTINI \(^17\)  | 0.978                                    | 6.78                              | 33                                 | 120                    | 1.356                                    |
| Morse-D \(^25\)  | 0.987                                    | 9.53                              | 66.2                               | 120                    | 1.542                                    |
| Morse-E (This work) | 0.978                                   | 10.29                             | 73.3                               | 120                    | 1.478                                    |

More properties of these CGMD models are estimated and compared with other widely used water models including the atomic models like SPCE and TIP3P. The results are shown in the Table 2. Note that, SPCE and TIP3P models have explicit oxygen and hydrogens, mW considers one water molecule as a single bead and the rest of the models consider 4 water molecules as a single bead.

The benchmarking studies to estimate the properties of water using various models at room temperature is performed and results are listed out in the table 2. The results show good performance of Morse based models and Morse-W4 does well in predicting surface tension. However, as the results suggest from higher temperatures, the Morse-D performs superior in comparison with the rest of the CGMD models.
Sensitivity of the time step of integration

The time step of integration is an indicator of the CGMD models’ sensitivity to represent the thermodynamic properties. To test this, the time step of CGMD models (MARTINI, Morse-D, Morse-E and Morse-W4) is varied from 2 fs to 62 fs and performed simulations for the lamellar system. This study is done for two temperatures (298 K and 373 K). The simulations start with a system equilibration for 50,000 steps using a time step of 20 fs and Nose Hoover thermostat. This step is followed by the production runs for 100,000 steps using corresponding time steps (\(dt\)) at micro–Canonical Ensemble (NVE). The resulting fluctuations in total energy and temperature is measured using the standard deviation of the data.

\[
SD(T) = \sqrt{\frac{\langle (T - \langle T \rangle)^2 \rangle}{N-1}}
\]

\[
SD(E) = \sqrt{\frac{\langle (E - \langle E \rangle)^2 \rangle}{N-1}}
\]

The results of the simulations and the fluctuations in temperatures are given in Fig. 5a (for 298 K), Fig. 5b (for 373 K) and the fluctuations in total energy are given in Fig. 6a (for 298 K) and Fig. 6b (for 373 K) respectively.

![Figure 5: Standard deviation of temperature for various CGMD models for varying time step of integration. The results are taken from the micro canonical ensemble (NVE) simulation of the lamellar system equilibrated at a) 298 K and b) 373 K. The markers indicate MARTINI model (square), Morse-D (triangle), Morse-E (diamond) and Morse-W4 (circle) models respectively.](image)

![Figure 6: Standard deviation of total energy for various CGMD models for varying time step of integration. The results are taken from the micro canonical ensemble (NVE) simulation of the lamellar system equilibrated at a) 298 K and b) 373 K respectively. The inset shows the zoomed in view for the timesteps after 25 fs, which indicate a diverging trend of standard deviation of total energy of the system. The markers indicate MARTINI model (square), Morse-D (triangle), Morse-E (diamond) and Morse-W4 (circle) models respectively.](image)
The sensitivity study results show that the MARTINI model has the highest fluctuations in both energy and temperatures. Moreover, the total energy diverges exponentially after 30 fs and the temperature diverges exponentially after 35 fs for MARTINI model. The fluctuations in total energy are small for Morse based models and hence the region from 25 fs to 62 fs is zoomed in (inset figures) for better clarity in Fig. 6a and Fig. 6b. For temperature fluctuations, Morse-D and Morse-E shows slightly better stability compared with Morse-W4. However, for total energy, Morse-W4 shows the best stability among the selected models.

Overall, Morse-W4 has a better stability among the four models in terms of energy and temperature fluctuations for micro canonical ensemble simulations and a time step of 40 fs or 50 fs can be used without any stability issues or divergence issues in energy and temperature of the system. The results also indicate that the previously developed Morse-D model is the best model among the four to represent the thermodynamic properties and is suitable for the evaporation studies for a wide range of temperatures.

Figure 7: Comparison of Morse-D model’s density (a), enthalpy of vaporization (b), and surface tension (c) with experimental data using a timestep of integration of 50 fs. The solid line indicates the experimental value as per NIST database and the blue shade indicates the 10% band. The standard deviation of simulation data is less than 2% in all cases and hence the error bars are not plotted.

At this point, since Morse-D is found to be a better choice due to its accuracy at higher temperatures, the results are reproduced for the temperatures from 280K to 500K.

Methods and tools used

All CGMD simulations are performed using the LAMMPS software, version 15th April 2020. For visualization Visual Molecular Dynamics (VMD) software is used. For CGMD simulations, a default time step of 20 fs is used unless otherwise specified. Python 3.9 programming language is used to create SPEA2 code, preprocessing and postprocessing tools for the CGMD simulations. C++ language-based library is developed and used for fast LAMMPS dump file reading and processing. A temperature of 293 K is used for Morse-E parameterization since it is the room temperature according to NIST standards. Temperature of 298 K is used to compare results with other water models. A temperature of 373 K is used to check the models at boiling point of water.

Nanopore Evaporation simulations

In this section we utilize the coarse grain water model Morse-D with a hydrophilic metallic nanopore to study the heat flux characteristics at nanopores. The cross-sectional view of the system considered for studying heat flux is shown in the Fig. 8. The solid region means the metallic region around the nanopore heating region. The reservoir will supply water to the nanopore, and the upper portion is for vaporization and condensation. The diameter of the pore is indicated as \( d \) and other relevant dimensions of the system is labelled and shown in the left. The diameter of the pore is changed from 2 nm to 4 nm and those molecular models are shown in the middle of Fig. 8. The heating of the pore region will help in evaporating the fluid as shown in the right panel of the Fig. 8. The region labelled as “heat flux region” is used to estimate the heat flux of the system and the heating region is the region of heat supply (in this case constant temperature).
Figure 8: In-Silico system setup for estimating the evaporative heat flux in nanopores. The conceptual 2D layout of the periodic system with dimensions are shown on the left. The images of the molecular model with various nanopore diameters are shown in the middle. The heat flux estimation region, cooling region and the flow of the fluid in the system is shown in the schematic (right).

The number of water (Morse-D) beads in the system varied between 2200 to 5000 across the systems to ensure there are enough water beads in the reservoir after wetting the nanopore. The walls of the solid material are made with single layer simple cubic structure with a spacing of 0.5 nm between the beads in all directions. The cutoff radius of the force field is 1.2 nm, which is almost equal to the distance between the adjacent water beads and second layer of solid and hence the attractive contribution will be negligible due to the second and third layers of solid beads. This is the reason why the nanopores are modeled as shown in the Fig. 8 (in middle) with single layer solid beads. The water beads and solid beads interact through a Lennard-Jones potential (Eqn. 9) with $\epsilon = 0.47 \text{ nm}$ and $\sigma = 0.5 \text{ kcal/mol}$ corresponding to a hydrophilic surface 25.

$$E_{LJ} = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]$$  \hspace{1cm} (9)

Here, $\epsilon$ is the depth of the energy well, $\sigma$ is the equilibrium distance of beads and $r$ is the inter bead spacing The heat flux in a periodic system is estimated as per Eqn. 10.

$$\vec{J} = \frac{1}{V} \left[ \sum_i \vec{v}_i \epsilon_i + \frac{1}{2} \sum_{\langle i,j \rangle} \vec{F}_{ij} (\vec{v}_i \cdot \vec{F}_{ij}) \right]$$  \hspace{1cm} (10)

Here, $\vec{J}$ is the heat flux vector, $V$ is the volume of the control volume under consideration, $\vec{v}_i$ is the velocity and $\epsilon_i$ is the unit vector of the $i^{th}$ particle. The term $\vec{r}_{ij}$ is the particle separation and $\vec{F}_{ij}$ is the force between $i^{th}$ and $j^{th}$ particles.

**Methods and tools used**

The periodic system mentioned in Fig. 8 is modeled using a Python script with appropriate dimensions and inter-bead spacings. The diameter of the nanopore was changed as 2 nm, 3 nm and 4 nm. The nanopore region and the region just above it is used for heating and let’s call it as heating region. The 3 nm thick region just above the nanopore is used for estimating the heat flux due to evaporation. Simulations are performed using the software LAMMPS 31. The timestep of integration is 50 $f_s$, cutoff radius of 1.2 nm, and the system was equilibrated for 1.25 ns at 300 K. The temperature of the heating region is then connected to a Langevin thermostat which raises the temperature from 300 K to 600 K and ran for 30 million steps (1.5 $\mu$s). The temperature increment rate was 200 K/$\mu$s. The vertical ($z$-axis) component of the heat flux ($J(z)$) is estimated every 0.25 ps and written to a file for postprocessing. A python script is used to process the file to estimate the actual temperature in the heating region, temperature in the flux region, and heat flux after temporally averaging at four chunks of simulation time. The temperature difference between the temperature of the heat flux region and the temperature of the nanopore (heating region) is called as wall superheat is an important measure of dry out during evaporation.
Figure 9: The estimated heat flux for the nanopores is shown for diameters 2 nm, 3 nm, and 4 nm. (a) The heat flux is shown against the wall superheat for all three cases. (b) Both nanopore (wall) temperature and heat flux region (flux) temperatures are shown against the heat flux for the 4 nm case.

Wall superheat is estimated from simulations as $T_{ws} = \langle T_{HF} \rangle - \langle T_{NP} \rangle$, where $T_{ws}$ is the wall superheat, $T_{HF}$ is the ensemble averaged temperature of the heat flux region and $T_{NP}$ is the temperature of the nanopore. The estimated heat flux along the z-axis is plotted for all the cases against the wall superheat in the Fig. 9. The results shows that the critical nanopore for evaporation is in between 3 nm and 4 nm. The heat flux is estimated to be in the range of 250~700 $W/cm^2$ for the 4 nm case, gradually increasing with temperature.

For the cases of 2 nm and 3 nm, the wall superheat is very high and corresponds to the dry out region in pool boiling experiments. The heat flux estimation using molecular simulations include the contribution of force of attraction term and hence the value can become negative when inter-bead (molecular) attraction dominates advection term. This is the reason why the heat flux is shown as negative for the $d = 2$ nm case. The cooling region is required to remove any unwanted heating of the reservoir liquid, since the evaporated molecules come back to reservoir due to periodic boundary condition. This cooling however will not affect the physics behind the nanopore evaporation because the cutoff radius is an order of magnitude less than the vapor region length.

Discussion on results and future directions

The inspiration to develop Morse potential based CGMD models was due to the undesirable artifacts produced by Lennard-Jones based models and promising the prior work by Molinero and team. Following their route, I have fine-tuned the force field properties using machine learning techniques. I optimized the Morse based model for matching the enthalpy of evaporation, surface tension and density at room temperature. However, one important property of the fluid called self-diffusion coefficient was left out. After optimizing the Morse-E, while comparing the results, I found that Morse-D, a model that was done 2 years ago is better at representing the water properties at higher temperatures. Hence Morse-D was used for the evaporation studies.

The nanopore evaporation study shows the critical diameter for the inception of evaporation in nanopores is 4 nm. This study can be elaborated in detail regarding the pressure distribution, velocity profile of the fluid flow, temperature distribution etc. are interesting to know. Since the pressure variations in the nanopores are dominated by long range electrostatic forces, studies can be done to address it while performing evaporation simulations.

Conclusions

In this study a coarse-grained water model at room temperature is developed using Morse potential at room temperature. The developed model (Morse-E) is not so superior in reproducing the thermodynamic properties in comparison with Morse-D. The Morse-D water model which accurately predicts the water properties at higher temperatures is used to study the evaporation from hydrophilic nanopores. The results show that 4 nm is the critical diameter to initiate continuous evaporation at nanopores. The proposed water CGMD model has very good numerical stability at higher time step of integration and hence can perform longer simulations. This is a first of a kind insight into nanopore evaporation and serves as the basis for performing nanopore evaporation studies in complex networks.
Author Declaration
The author declares no competing financial interest.

Supplementary Information
Supporting information is freely available at .

The supporting document consists of estimation of computational time requirement for droplet evaporation using MD simulations, validation of SPEA-2 method implementation, and Nelder-Mead method optimization of lamellar system.

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