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Research paper

Calculating free energy profiles using entropy as a reaction coordinate: Application to water nucleation

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A R T I C L E I N F O

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We identify the nucleation pathway for a liquid droplet of a water-like system. In order to calculate the free energy barrier associated with the droplet formation, we use the recently developed μVT-S simulation method to unravel the nucleation process. We analyze the interdependence between droplet size, entropy and free energy of nucleation. Three key features emerge: the droplet size increases as entropy decreases during the process, the nucleation free energy increases as supersaturation decreases, and the nucleation free energy increases as T decreases. This method can be readily applied to calculate free energy barriers of activated events with entropy as the reaction coordinate.

1. Introduction

The nucleation of a liquid droplet from a supersaturated vapor is a phenomenon of great fundamental and technological importance in chemistry, physics and materials science and engineering [1–5]. For instance, the nucleation of water droplets is central to atmospheric physics and chemistry [6–9]. Nucleation has, however, remained challenging to model and simulate, since nucleation is an activated process, associated with a very large free energy barrier that the system has to overcome to give rise to a droplet of a critical size. The large nucleation free energies result from the competition [10] between an energetically unfavorable term, corresponding to the formation of the interface between the parent and emerging phase, and of a favorable term, stemming from the conversion of the metastable parent phase to the new stable phase. While developments in the classical nucleation theory [11] and simulation studies [7,8] have allowed to accurately predict many features of this process, the impact of the conditions still remains an open question [12–14].

In this work, we focus on determining the isothermal nucleation pathway for the formation of a liquid droplet. In terms of statistical ensemble, the grand-canonical (μVT ensemble) is a natural way to model an isothermal nucleation process. In particular, we take advantage of a method recently developed in the group, known as the μVT-S method [15–17], which uses the entropy of the system as the reaction coordinate for the nucleation process, simulated in the grand-canonical ensemble. As a test case, we consider the core-softened water (CSW) potential [18–21] for a water-like system and simulate the nucleation of a droplet for this model. Core-softened potentials have become increasingly popular in recent years in modeling fluids with anomalous properties. These potentials consist in pairwise isotropic interactions which have been shown to be suitable to model the complex phase behavior of a wide range of systems [22–26], including e.g. liquid metals as well as the phase behavior of water. In particular, recent work has shown that the CSW potential could be successfully used to obtain specific features of water [27–29] including the density maximum exhibited by liquid water at low temperature and provided, a way to model both the vapor-liquid critical point and a liquid-liquid phase transition [30–32].

The paper is organized as follows. In the next section, we discuss the simulation method used to obtain the nucleation pathway and introduce the CSW model, as well as other technical details necessary to carry out the simulations. We then, present the results obtained for the isothermal nucleation process. More specifically, we provide the free energy profile of nucleation for different supersaturations and shed light on the interplay between the size of the nucleus and the entropy of the system throughout the nucleation process. We also discuss the impact of temperature on the height of the free energy barrier of nucleation, when the supersaturation is held fixed. We finally draw the main conclusions from this work in the last section.

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Table 1
CSW water at $T = 515.31$ K: Data at coexistence (Coex) and for the thermodynamic conditions of nucleation for 3 different supersaturations (Systems 1, 2 and 3).

	μ (kJ/kg)	$\Delta\mu$ (kJ/kg)	P (bar)	P/P_{coex}	S_l (kJ/kg/K)	S_v (kJ/kg/K)
Coex	−2892.8	–	81.88	1.0	4.550	6.109
System 1	−2872.8	20.0	204.51	2.5	4.488	–
System 2	−2866.4	26.4	246.25	3.0	4.469	–
System 3	−2860.2	32.6	286.81	3.5	4.452	–

Table 2
Thermodynamic conditions for the nucleation of *CSW* water for different temperatures (Systems A, B and C).

	T (K)	μ (kJ/kg)	$\Delta\mu$ (kJ/kg)	P (bar)	P/P_{coex}
System A	515.31	−2860.2	32.6	286.81	3.5
System B	486.68	−2734.8	32.4	268.25	4.5
System C	458.05	−2610.3	34.8	273.31	6.5

2. Simulation method

2.1. CSW model for water

In the CSW potential [18,19,21], water molecules are modeled with a single interaction site and the interactions between different water molecules is calculated according to:

$$U_r = \frac{U_R}{1+\exp(\Delta(r-R_R)/a)} - U_A \exp\left[-\frac{(r-R_A)^2}{2\delta_A^2}\right] + U_A\left(\frac{a}{r}\right)^{24} \qquad (1)$$

The three terms in this sum consist of (i) a soft repulsive shoulder of height U_R, such that $U_R/U_A = 2$, (ii) an attractive Gaussian well of depth U_A and width $2\delta_A\sqrt{2\ln 2}$, with $(\delta_A/a)^2 = 0.1$, and (iii) of a steep repulsive part. The remaining parameters $\Delta = 15$, $R_R/a = 1.6$ and $R_A/a = 2$ control the shape and steepness of the interaction potential. We then apply the following scaling factors for the energy $U_A/k_B = 7.90142 \times 10^{-21}$ J, the length $a = 1.9673$ Å, and for the mass $m = 18$ g/mol. The cutoff for the calculation of the interaction energy was set to $3a$ and we did not apply any long-range corrections beyond this cutoff. We add that, with the use of the scaling factors U_A, a and m, the CSW model leads to a critical point of $T_c = 647$ K, $\rho_c = 0.322$ g/cm^3 and $P_c = 22$ MPa in excellent agreement with the experimental data [33]. Furthermore, recent work has shown that core-softened models capture both the static and dynamic anomalies of water [34,35].

2.2. Determining the nucleation pathway: μVT-S simulations

We start by explaining how we determine the isothermal nucleation pathway using μVT-S simulations. We only briefly outline the method as more details can be found in the original work [15–17]. Carrying out simulations in the grand-canonical ensemble, i.e. at constant chemical potential μ, volume V and temperature T, provides a convenient way to calculate the molar entropy S of the system during the course of the simulation through

$$S = \frac{U-A}{T} \qquad (2)$$

where U is the molar internal energy, obtained by adding the potential and kinetic energy, and A is the molar Helmholtz free energy of the system (see our previous work [17], as well as the work of Waghe, Rasaiah and Hummer [36], for more details). This equation implies that the entropy S of the system can be used as an order parameter or reaction coordinate to study a nucleation event and to drive the formation of the new liquid phase from the metastable

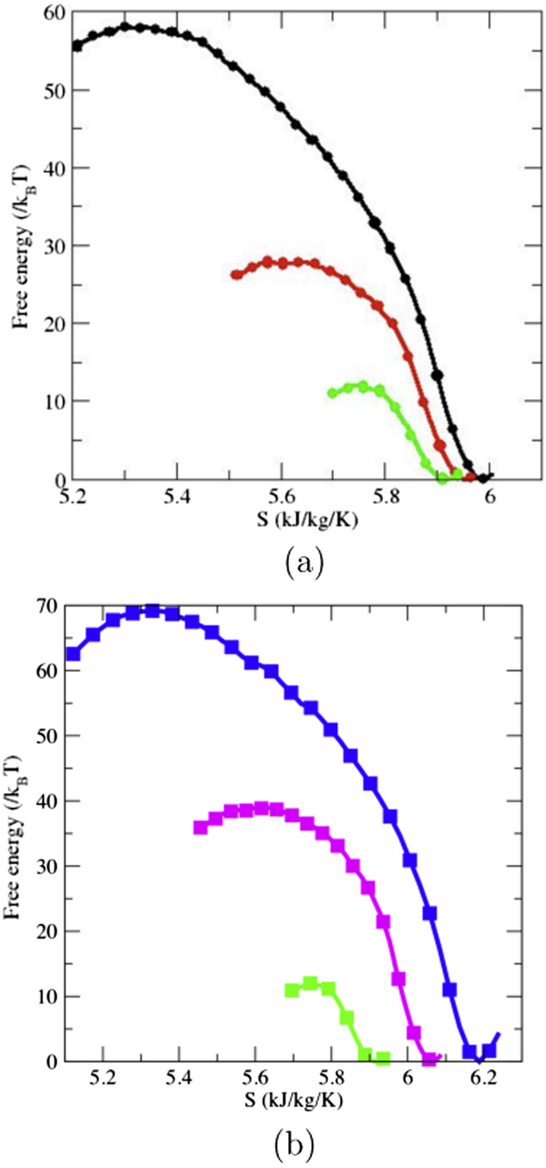

Fig. 1. Free energy vs. entropy at (a) $T = 515.31$ K for Systems 1 (black), 2 (red) and 3 (green), and (b) for temperatures ranging from $T = 515.31$ K (System A in green), $T = 486.68$ K (System B in magenta) and $T = 458.05$ K (System C in blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)