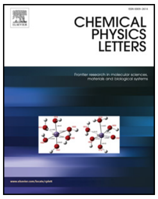
Chemical Physics Letters 713 (2018) 85–90

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett



Research paper

Molecular dynamics simulation of bubble nucleation in two-component Lennard-Jones solutions

V.G. Baidakov*, V.M. Bryukhanov

Institute of Thermal Physics of the Ural Branch of the Russian Academy of Sciences, Amundsen st. 107a, Ekaterinburg 620016, Russia

HIGHLIGHTS

- Nucleation of bubble in two-component Lennard-Jones solutions is investigated.
- The method of molecular dynamics (MD) simulation is used.
- The results of simulation are compared with classical nucleation theory (CNT).
- The effect of the size of a critical bubble and its composition on the value of surface tension is discussed.

ARTICLE INFO

Keywords:
Bubble nucleation
Classical nucleation theory
Lennard-Jones solution
Molecular dynamics simulation
Surface tension of bubbles

ABSTRACT

We present the results of molecular dynamics (MD) studying of bubble nucleation in binary Lennard-Jones (LJ) solutions modelling a methane–nitrogen system. The mean lifetime method is used in systems containing 12000–1024000 LJ particles at temperatures $T^* = k_B T/\varepsilon_{11} = 0.85$, 1.0 and 1.1 to determine the dependence of the nucleation rate J on the pressure and concentration of a solution. The results of simulation are compared with classical nucleation theory (CNT). The effect of the size of a critical bubble and its composition on the value of surface tension is discussed.

1. Introduction

A first-order phase transition presupposes the existence of metastable states. A superheated (stretched) liquid whose decay is connected with the formation and growth of vapor nuclei (bubbles) is a particular case of a metastable state. Liquid superheatings are observed in intensifying the processes of heat and mass transfer in power-generating equipment [1], water desalination plants [2], geysers and active volcanoes [3], in developing gas-condensate deposits [4], etc.

Processes of nucleation in superheated (stretched) one-component liquids have been investigated both by experiment [5–8] and in molecular dynamics (MD) simulation [9–15]. The MD method opens up considerable opportunities in studying homogeneous nucleation and makes it possible to determine not only the parameters of nucleation that are registered in experiment (superheating temperature, tensile stress and nucleation rate), but also quantities that are as yet inaccessible to direct measurements, namely, the size of a critical nucleus, its thermodynamic properties and structure, the nucleus size distribution function, etc.

Investigations of the kinetics of spontaneous boiling-up of simple one-component liquids (see the monograph [8] and references to it) have revealed a systematic discrepancy between experimental data and classical nucleation theory (CNT): superheatings achieved by experiment are always lower than their theoretical values. This result is also confirmed by MD simulation [14,15]. It is shown [14] that the disagreement between CNT on the one hand and experimental data on the other, is connected with the neglect in CNT of the size dependence of the properties of new-phase critical nuclei. The surface tension of vapor bubbles in a simple one-component liquid is smaller than at a plane liquid-vapor interface.

In experiments on krypton-argon [16] and ethane-nitrogen [17] solutions it has been established that additions of the substance being dissolved (the second component) into the solvent reduce the discrepancy between CNT and experiment data in the superheating temperature, and close to the equimolar composition one can observe “superheating” beyond theory. The reasons for this may be the effect of the composition on the size dependence of the surface tension of critical bubbles, the relaxation processes connected with the establishment of thermal and mechanical equilibria in a bubble and adsorption equilibrium at its interface (the effect of dynamic surface tension), etc. The

---

* Corresponding author.
E-mail address: baidakov@itp.uran.ru (V.G. Baidakov).

https://doi.org/10.1016/j.cplett.2018.10.010
Received 16 August 2018; Accepted 4 October 2018
Available online 05 October 2018
0009-2614/ © 2018 Published by Elsevier B.V.

fact that additions of a more volatile component into the liquid lead to an increase in the surface tension of critical bubbles and a decrease in the discrepancy between the values of the solution surface tension at a plane and a curved interface is shown in the framework of the van der Waals gradient theory [18]. At the same time, MD simulation [19] points to a considerable increase in the time of the establishment of equilibrium at a solution-gas interface as compared with a pure liquid–vapor one.

In this paper we present the results of MD simulation of the process of spontaneous boiling-up of a two-component Lennard-Jones (LJ) solution that simulates a methane-nitrogen system. Calculations were made in the temperature range between the triple and the critical point of the solution. Using the method of the mean lifetime of a metastable system [5], we calculate the nucleation rate, compare the data obtained with CNT, whence we determine the surface tension of critical bubbles and their size, temperature and concentration dependences. The data obtained are analyzed in the context of the Gibbs and van der Waals theories.

2. Classical theory of nucleation in binary solutions

2.1. Critical nucleus and the work of its formation

The decay of a metastable system begins with the formation and subsequent growth of a critical nucleus. If the thermodynamic state of the initial environment does not change ($T, p = \text{const}$) as a result of the appearance of a new-phase nucleus, the work of formation of a critical nucleus is numerically equal to the height of the Gibbs free energy barrier ΔG_*, which must be overcome by means of fluctuations, and may be presented as [20].

$$W_* = \Delta G_* = \frac{16\pi}{3}\frac{\gamma^3}{(p'_* - p)^2} = \frac{4}{3}\pi R_*^2\gamma = \frac{2}{3}\pi R_*^3(p'_* - p), \tag{1}$$

where γ is the surface tension at the nucleus-metastable phase interface, p'_* is the pressure in a critical nucleus, and R_* is its radius. In CNT the value of γ is taken equal to its value at a flat interface. The quantities without primes refer to liquid, those with primes, to vapor. The lower index * indicates that the quantity belongs to a critical nucleus. The surface of tension is taken as the dividing surface.

Next we examine the boiling-up of a superheated (stretched) binary solution. All the values included in Eq. (1) characterize the solution.

A critical bubble is in mechanical and real equilibrium with the solution that surrounds it. The conditions of this equilibrium will look like:

$$p'_* = p + \frac{2\gamma}{R_*}, \tag{2}$$

$$\mu'_\alpha(p'_*, T, c'_*) = \mu_\alpha(p, T, c), \qquad \alpha = 1, 2. \tag{3}$$

Here c is the mole fraction of the second component. The function $\Delta G(R, c')$ close to the equilibrium state is a surface of double curvature. The equilibrium is stable against variations in the bubble composition, but unstable against changes in its size. At given temperature T, pressure p and concentration c of the solution Eqs. (2) and (3) determine the radius R_* and the composition c'_* of an equilibrium bubble.

In the case of small superheatings, far from the line of critical points, a liquid solution may be considered incompressible and the vapor in a bubble an ideal gas. Then for the pressure and the concentration in a critical bubble we have [8]

$$p'_* = p_s\left[c'_s \exp\left(-\frac{p_s - p}{p_s}\cdot\frac{v_1}{v'}\right) + (1 - c'_s)\exp\left(-\frac{p_s - p}{p_s}\cdot\frac{v_2}{v'}\right)\right], \tag{4}$$

$$c'_* = c'_s\left[c'_s + (1 - c'_s)\exp\left(\frac{p_s - p}{p_s}\cdot\frac{v_1 - v_2}{v'}\right)\right]^{-1}, \tag{5}$$

where p_s and c'_s are the saturation pressure and the equilibrium vapor composition at a plane interface, v_α is the specific partial volume of the α-th component, and v is the specific volume of the solution.

2.2. Nucleation rate

The problem of description of the initial stage of a phase transition in a multicomponent mixture was first considered by Reiss [21], Nesis and Frenkel [22]. Using the Volmer-Zeldovich-Frenkel approach [23–25], Nesis and Frenkel [22] derived an expression for the nucleation rate on the assumption that the factor determining the dynamics of the bubble growth is the rate of the liquid evaporation into a void. A more complete solution of the problem of nucleation in a superheated solution, which takes into account the molecular and the diffusion supply of a substance, the viscous and inertial forces that manifest themselves during the evolution of a bubble, and also the thermal conditions at its boundary, is given in paper by Baidakov [26,8]. The expression for a stationary flow of nuclei (nucleation rate) in a two-component system has a form similar to that of a one-component medium:

$$J = \rho\,\lambda_0 R_*^2\left(\frac{k_B T}{\gamma}\right)^{1/2}\exp\left(-\frac{W_*}{k_B T}\right) = \rho B \exp\left(-\frac{W_*}{k_B T}\right). \tag{6}$$

Here ρ is the number of molecules in a solution unit of volume of the metastable phase, λ_0 is the decrement of increase of an unstable variable, k_B is the Boltzmann constant and B is the kinetic factor determining the average rate of the bubble transition over the critical size. The value of $\rho\exp(-W_*/k_B T)$ in the right-hand part of (6) is the average number of critical nuclei in a unit of volume.

The value of B changes little with an increase in the solution superheating (stretching). Therefore in calculations of the kinetic factor the size dependence of the properties of new-phase nuclei may be neglected. The effect of the liquid viscosity and sluggishness, the heat supply and some other factors on the bubble growth rate close to the critical size depends on the substance and the thermodynamic state at which the nucleation proceeds. In the bubble dynamic equation the inertial terms may be neglected if $\chi = \rho\,\gamma R_*/8\eta^2 < < 1$, where η is the solution viscosity. Our MD calculations were made at negative pressures. Here for a Lennard-Jones solution the value of χ does not exceed 0.2.

At $p < 0$ the bubble is practically free from particles of the solvent and the solute, and its growth is mainly retarded by viscous forces. According to [8], when $\omega = 3v_t\eta/2\gamma > > 1$ and $\omega' = R_* p'_*/v_t\eta < < 1$, and $\beta = v_t R_*/4k_B T D\rho H < < 1$, where v_t is the thermal velocity of particle motion, D is the diffusion coefficient, and H is the Henry constant, for the kinetic factor in (6) we have

$$B = \frac{\rho R_*}{2\eta}(k_B T\gamma)^{1/2}. \tag{7}$$

In our MD simulation $\omega = 2\text{–}8$, $\omega' = (2\text{–}200)\cdot 10^{-3}$, $\beta = 0.3\text{–}0.9$, i.e., strictly speaking, the criteria substantiating the use of the approximation (7) have not been met. Nevertheless, the limiting case (7) is nearest the general solution, which takes into account all the factors that influence the dynamics of the bubble growth in the solution. It should be noted, that owing to the extremely strong T, p and c dependence of the exponential factor, the effect of the differences between the numerical values of B obtained in different limiting cases on the value of the limiting superheating (stretching) of the solution proves to be relatively small.

3. Molecular dynamic simulation

3.1. Model

The Large-scale Atomic/Molecular Massively Parallel Simulator

Download English Version:

https://daneshyari.com/en/article/11553595

Download Persian Version:

https://daneshyari.com/article/11553595

Daneshyari.com