



## Research paper

## Bubble nucleation in a Lennard-Jones binary liquid mixture



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## ABSTRACT

We report a molecular dynamics (MD) study of homogeneous bubble nucleation in a stretched Lennard-Jones binary mixture at a temperature close to the solvent triple point. The pressure of the limiting stretching  $p_n$  corresponding to a fixed value of the nucleation rate has been determined. The values of  $p_n$  achieved in MD simulation are lower than those calculated from classical nucleation theory (CNT). The discrepancy between the data of MD simulation and CNT may be connected with the neglect in the latter of the size dependence of the surface tension of critical bubbles.

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## 1. Introduction

In many natural and technological processes with the participation of fluid phases the latter are mixtures of substances. The presence in a system of several components changes essentially its thermodynamic behavior. Additional thermodynamic degrees of freedom lead to new phase transitions, there appear critical points of higher order, and nucleation becomes multidimensional [1,2].

During the boiling-up of a liquid mixture the state of a vapor-phase nucleus will be determined not only by its size, but also by the partial pressures of the mixture components in the bubble. The dynamics of the bubble growth, the trajectory of its motion through the saddle point of the activation barrier, which separates a homogeneous metastable state from a stable two-phase one, will depend on the rate of supply of each of the mixture components into the bubble, viscosity, thermal conductivity and some other parameters of the solution.

One of the approaches to the study of nucleation that have been widely used in recent years is molecular dynamics (MD) simulation [3–5], which makes it possible, along with obtaining quantitative characteristics of the nucleation process, to visualize it and to separate distinctly homogeneous and heterogeneous nucleation, which is not always possible in experiments. As distinct from experiments, which usually register only the dependence of the nucleation rate on thermodynamic state parameters, MD simulation is capable of determining the size of a critical nucleus, the work of its formation, the nucleus growth rate and some other

parameters. Thus, it becomes possible to test classical nucleation theory (CNT) not only by the final result, but also in detail.

The present paper is devoted to MD simulation of nucleation in a stretched (superheated) Lennard-Jones (LJ) liquid mixture. Bubble nucleation has been investigated at sufficient length in one-component liquids [6–10]. Much less attention has been given to the study of bubble nucleation in liquid mixtures [11–13].

The subject of our investigation is a liquid mixture with complete solubility of the components. In MD simulation we calculate the main characteristics of the nucleation process and compare them with CNT.

## 2. Molecular dynamics model and the results of calculations

The system under investigation contained  $N = 32,000$  LJ particles. The particles were located in a cubic cell with periodic boundary conditions. The potential parameters  $\sigma_{11}$ ,  $\epsilon_{11}$  and the particle mass  $m_1$  of the solvent were used as units of reduction of the quantities being calculated. The solute had a smaller value of the energy parameter of interparticle interaction ( $\epsilon_{22}/\epsilon_{11} = 0.6414$ ), approximately equal sizes of particles ( $\sigma_{22}/\sigma_{11} = 0.9688$ ) and a much larger mass of them ( $m_2/m_1 = 1.746$ ). A system with such parameters is a model of a methane–nitrogen solution. The parameters of the potential for methane and nitrogen were taken from Ref. [14]. The cross interaction parameters were calculated by the Berthelot  $\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}$  and Lorentz  $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$  rules. In molecular dynamics simulation the integration step of equations of motion was taken equal to 0.002318 (in units of  $(m_1\sigma_{11}^2/\epsilon_{11})^{1/2}$ ). The cutoff radius of the LJ potential was  $r_c = 6.78\sigma_{11}$ . A solution of a

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prescribed concentration was prepared by replacing an appropriate number of the solvent particles with those of the solute.

All calculations were made at a reduced temperature  $k_B T / \varepsilon_{11} = 0.7$ . The method of mean lifetime measurement was used to determine the nucleation rate  $J$  [15]. An isothermal penetration into the region of metastable states of a mixture was realized by decreasing the density by way of an overall stretching of the cell and scaling of the particle coordinates. At given temperature and composition the interval of density (pressure) was determined in which the expectation time for solution boiling-up was within the limits of 100–800 reduced units. Then in the interval indicated several values of density were fixed, and the mean expectation time for the appearance of the first viable bubble  $\bar{\tau}$  was determined from the results of 100–200 boiling-ups of the liquid phase. It is related to the nucleation rate by the relation  $J = (\bar{\tau}V)^{-1}$ , where  $V$  is the volume of a metastable liquid.

The results of calculating the pressure dependence of the nucleation rate along the lines of constant values of the concentration of the second component  $x$  are given in Fig. 1. The data of Refs. [9,10] are presented for a pure solvent and substance dissolved.

Fig. 2 shows the pressure of the limiting stretching  $p_n$  that corresponds to a nucleation rate  $J = 2 \cdot 10^{-7}$  (in units of  $\sigma_{11}^4 (\varepsilon_{11}/m_1)^{1/2}$ ). An increase in the concentration of the substance being dissolved in a mixture reduces the value of the limiting stretching. The phase equilibrium pressure  $p_s$  and the surface tension  $\gamma_\infty$  of a methane–nitrogen solution have been obtained by MD simulation of a two-phase liquid–gas system with a plane interface. The computational procedure is described in detail in Ref. [16].

### 3. Comparison of the data obtained with classical nucleation theory

According to CNT the stationary nucleation rate is determined by the expression [17–19]

$$J = \rho B \exp(-W_*/k_B T), \quad (1)$$

where  $\rho$  is the density of a metastable solution,  $B$  is the kinetic factor dependent on the average rate of nucleus transition through the critical size, and  $W_*$  is the work of formation of a critical nucleus.

In the case of formation of a bubble in a stretched liquid at pressure  $p$  and temperature  $T$

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

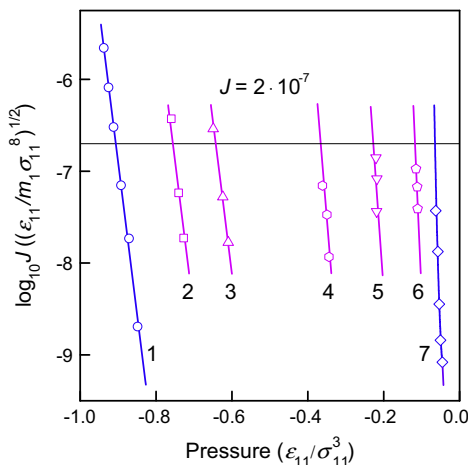


Fig. 1. Logarithm of the bubble nucleation rate as a function of pressure at  $T=0.7$  and the molar fraction of the second component: (1)  $x=0$ ; (2) 0.1; (3) 0.2; (4) 0.5; (5) 0.7; (6) 0.9; (7) 1.0.

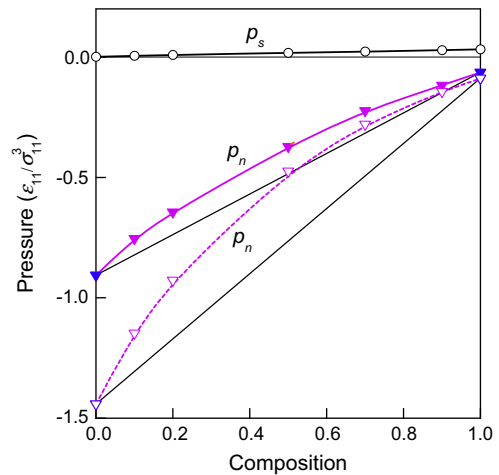


Fig. 2. Pressure of the limiting stretching of a liquid mixture at  $T=0.7$  and  $J = 2 \cdot 10^{-7}$  by the results of MD simulation (solid line) and CNT (dashed line).  $p_s$  is the pressure of phase equilibrium. Thin solid lines shown additive approximation.

where  $\gamma$  is the surface tension at the bubble–solution interface,  $p'_*$  is the pressure in a critical bubble,  $R_*$  is the radius of critical bubble determined from the condition of bubble mechanical equilibrium in liquid.

At temperatures remote from that of the critical point, when the number density of a liquid solution  $\rho$  exceeds considerably the density of a vapor–gas mixture  $\rho'$ , assuming the vapor–gas mixture in the bubble to be ideal and the liquid solution to be incompressible, one can write  $p'_* \cong p + (p_s - p)(1 - \rho'/\rho)$ ,  $x'_* \cong x'_s$ , where  $x'_s$  is the concentration of the second component in a critical bubble,  $x'_s$  is the molar fraction of the second component in a vapor–gas mixture at a flat interface [19]. In our case the solution temperature is close to the temperature of the solvent triple point. At  $x=0$ ,  $p_s \cong 0.001$ , and at  $x=1$ ,  $p_s \cong 0.024$ , i.e., practically, a critical bubble contains neither solvent particles nor particles of the substance dissolved. The bubble growth will be restrained by only the forces of viscous friction, and for the kinetic factor one can write [19,20]

$$B = \frac{\rho R_*}{2\eta} (k_B T \gamma)^{1/2}, \quad (3)$$

where  $\eta$  is the solution viscosity.

The pressures of limiting stretching calculated from Eqs. (1)–(3), which correspond to a nucleation rate  $J = 2 \cdot 10^{-7}$ , are shown in Fig. 2 as a dashed line. An increase of the content of the solute in the solvent leads to decreasing discrepancies between the results of CNT and MD simulation. For a pure solvent the disagreement in  $p_n$  is equal to 37%, for a pure solute it is 28%. According to additivity law,  $p_n(x) = p_n(0)(1-x) + p_n(1)x$ . The values of  $p_n$  obtained from CNT deviate from this law much stronger than the data of MD simulation.

If stretchings achieved in MD simulation are fixed, and the nucleation rates corresponding to them are compared with those calculated from CNT, then at  $x=0$ ,  $J_{MD}/J_{CNT} \approx 4 \cdot 10^9$ , and at  $x=1$ ,  $J_{MD}/J_{CNT} \approx 1 \cdot 10^4$ .

The pre-exponential factor in Eq. (1) depends only slightly on the temperature, pressure, and concentration. At  $x=0$  and  $x=1$  the value of  $\rho B$  is equal, respectively, to 0.40 and 0.25 and varies approximately linearly with the composition. The small difference in the values of  $\rho B$  between the solvent and the solute means that to a fixed value of the nucleation rate corresponds an approximately constant value of the reduced work of formation of a critical

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