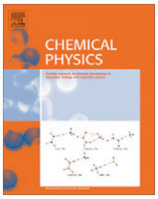
Chemical Physics 381 (2011) 44–48

Contents lists available at ScienceDirect

Chemical Physics

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



# Size dependence and effect of potential parameters on properties of nano-cavities in liquid xenon using molecular dynamics simulation

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ARTICLE INFO

*Article history:*
Received 27 July 2010
In final form 13 January 2011
Available online 20 January 2011

*Keywords:*
Molecular-dynamics
Lennard–Jones liquid
Nano-cavity

ABSTRACT

We have investigated the size dependence of a nano-cavity properties produced in a Xe fluid using molecular dynamics simulations. We have created a nano-cavity of different sizes at 170 and 200 K (cavities diameters are within 1–10 nm). Liquid pressure, vapor pressure and surface tension of the nano-cavity for some given values of diameter are calculated. Within 1–10 nm cavity diameter, we have observed two opposite behavior for dependency of surface tension on the cavity diameter: for the range of 1–5 nm, it increases with the diameter, while, for the range of 5–10 nm remains constant. Also, the value of liquid pressure becomes less negative, when the size of cavity increases. Vapor pressure in the cavity was found to be independent of cavity size.

In this paper, we have also studied the effects of Lennard–Jones potential parameters on the surface tension (while temperature and cavity radius are held constant).

## 1. Introduction

Nanoscience and nanomaterials have been identified world widely as the key to unlocking a new generation of devices with revolutionary properties and functionalities [1].

Cavitation is one of the fundamental phenomena in fluid mechanics. This phenomenon is often observed in pumps, orifice, venture tube, liquid jet where high-speed liquid flows occur, and is also observed in fluids in an acoustic field. Although cavitation has many negative aspects such as decline of performance and vibration in pumps, erosion on a solid surface and noise. Recent studies suggest that this phenomenon can also provide valuable applications for cleaning and medical purposes. Now a better understanding and the control of the cavitations process are strongly required, and they will enable us to design more reliable fluid machinery and to develop new techniques [2]. Micro-cavities have recently gained much attention in many fields. In particular, cavities with size of sub-micrometer, or “nano-cavity”, have become an attractive research target, partly because of recent technological progress of micro-cavity generations and partly in prospect of their fruitful applications, such as sensors and optical treatments. However, experimental investigation of their physical properties is far behind the applications due to their size and fragileness [3]. For example, controlling the cavitation process is related to designing a high-performance ship propeller. From scientific point of view, the cavitation is understood as a typical example of nucleation processes, and is related to thermodynamic properties and the limit of metastable liquid. From a microscopic viewpoint, despite this importance, less attention has been paid to cavitation and properties of liquid under negative pressure [4]. Recently, many works have done in this area [4–10].

In 2008, Matsumoto et al. investigated size dependence of surface tension nano-bubble in argon liquid. They showed that surface tension evaluated with assumption of the Young–Laplace (Y–L) equation has minor dependence on the bubble radius, and agrees with the surface tension of a planer interface [3]. The Y–L equation describes the difference between inside pressure and outside pressure of a spherical cavity due to the surface tension. The Y–L equation is simply deduced from mechanical stability of a cavity. The pressure difference inversely increases with the cavity radius. The Y–L equation is [11,12]:

$$P_{\mathrm{vap}} = P_{\mathrm{liq}} + \frac{2\gamma}{R} \qquad (1)$$

where $P_{\mathrm{vap}}$ and $P_{\mathrm{liq}}$ are the pressure inside (vapor phase) and outside (liquid phase) of the cavity, respectively, $\gamma$ is the surface tension, and $R$ is the cavity radius. Comprehensive studies of the cavity, bubble, and droplet, have been carried out over the past decades [3,13–22].

We have carried out molecular dynamics simulation to obtain both $P_{\mathrm{liq}}$ and $P_{\mathrm{vap}}$ for a nano cavity with various sizes. Then by assuming Eq. (1), we have calculated the surface tension and investigated its size dependence. Also we have studied effects of

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0301-0104/$ - see front matter
doi:10.1016/j.chemphys.2011.01.007

**Table 1**
Calculated number density of liquid in the nano-cavity at $T = 170$ K and $T = 200$ K temperatures, when the total number of xenon atoms is 32,000. Percent deviation of the cavity diameter is given in parenthesis.

| Temperature (K) | Cavity diameter (nm) | Number density of liquid (nm$^{-3}$) |
|---|---|---|
| 170 | 1 (−3.30) | 12.578 |
| 170 | 2 (+3.38) | 12.876 |
| 170 | 3 (−3.09) | 13.058 |
| 170 | 4 (−2.75) | 13.174 |
| 170 | 5 (+1.02) | 13.290 |
| 170 | 6 (+1.32) | 13.389 |
| 170 | 7 (−1.57) | 13.439 |
| 170 | 8 (+1.35) | 13.463 |
| 170 | 9 (+1.00) | 13.480 |
| 170 | 10 (+0.70) | 13.492 |
| 200 | 1 (−1.94) | 9.946 |
| 200 | 2 (−2.56) | 10.244 |
| 200 | 3 (+1.31) | 10.426 |
| 200 | 4 (−2.30) | 10.575 |
| 200 | 5 (−1.60) | 10.658 |
| 200 | 6 (−2.01) | 10.741 |
| 200 | 7 (+1.08) | 10.807 |
| 200 | 8 (+1.41) | 10.857 |
| 200 | 9 (−1.28) | 10.890 |
| 200 | 10 (−1.01) | 10.915 |

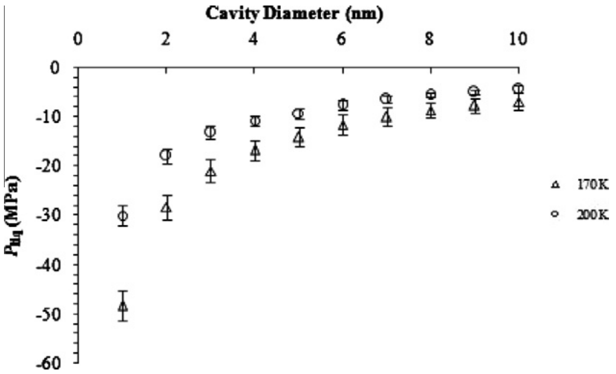

**Fig. 1.** Dependency of the liquid phase pressure on the cavity size (at $T = 170$ and 200 K) with the same number of particles ($N = 32{,}000$).

Lennard–Jones potential parameters ($\varepsilon, \sigma$) on the liquid pressure, vapor pressure and surface tension.

## 2. Molecular dynamics simulation

In this paper, the procedure used is similar to that introduced in references [3,4].

In the present study, molecular dynamics simulation on the bulk of liquid Xe was done using the DL-POLY-2.20 program [23]. Xenon particles are confined in a cubic cell with the three-dimensional periodic boundary conditions. We have performed the simulation on a FCC lattice of Xe atoms with LJ (12–6) parameters, $\sigma = 3.924$ Å and $\varepsilon = 2.1383$ (kJ/mol) [24].

$$V_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2}$$

The MD simulations are carried out in a *NVT* ensemble with a constant number of atoms *N*, volume *V*, and temperature *T* with the periodic boundary conditions. Xenon lattice has a FCC structure. A FCC block was first constructed from a FCC unit cell by replication in three dimensions with the center located at (0, 0, 0). The fractional coordinates in the FCC structure are (0, 0, 0), (0.5, 0.5, 0), (0.5, 0, 0.5), and (0, 0.5, 0.5). Temperature is controlled by a Nose–Hoover thermostat [25] and the equations of motion are integrated using the Verlet Leapfrog algorithm [26] with a time step of 0.001 ps. The system was equilibrated for 500 ps (500,000 time steps), the averages were computed over the next following 1 ns (10,00,000 time steps). The cutoff length is chosen to be 9 Å in the simulations. In these systems, the number of particles is $N = 32{,}000$. (To test that the system is equilibritated, we have plotted thermodynamic quantities such as potential energy and temperature as a function of time. When equilibrium is reached: the quantities should fluctuate around the average values and the averages should remain constant with time (no systematic drift).)

First, the system was equilibrated at a chosen temperature *T* with volume *V* corresponds to a normal liquid state (liquid without any cavities with pressure close to zero at the given temperature). Then, a spherical repulsive external force field has been applied at the central part of the cell to generate a tiny cavity. After the equilibrium is reached, the force field is removed [3]. With varying the system volume *V*, we can obtain a liquid containing a single cavity with various sizes. In this work, we have investigated the system at two different temperatures, namely 170 K and 200 K. (Xenon at these temperatures is in the liquid state, at ordinary pressures). Also, we have changed the Lennard–Jones parameters ($\varepsilon, \sigma$) in the force field file to investigate the effects of these parameters on liquid pressure, vapor pressure, and surface tension.

Several particles, which have been evaporated spontaneously, are inside the cavity.

The result for number density of the liquid for various cavity diameters at 170 K and 200 K is summarized in Table 1.

## 3. Results

In this study, the liquid pressure is calculated via the usual virial expression.

Pressure evaluated for the whole system was found to be almost equal to $P_{\mathrm{liq}}$ because the contribution of the cavity region is much smaller than that of the liquid region. The results are shown in Fig. 1.

The fact that creating a cavity inside a liquid requires transferring some molecules from the bulk to the surface, for which potential energy increases; therefore, some work has to be done. Such increase in the potential energy leads to a negative force and hence negative pressure. Transfer of a molecule from a large cavity surface to the liquid surface needs less work, compared to a small cavity. For instance, if surface of the cavity is large enough no significant work needed to transfer some molecules from its surface to the liquid surface. Therefore, we may expect that liquid pressure becomes a less negative value, when the size of cavity increases, as shown in Fig. 1. At lower temperatures, at which the liquid cohesive energy is more (stronger attraction among the molecules), we may expect that the transfer of a molecule from the cavity surface to the liquid surface requires more reversible work; as a result, the liquid pressure becomes a larger negative number, as shown in Fig. 1.

For calculation of vapor pressure ($P_{\mathrm{vap}}$), we have used the empirical equation of state for gaseous Xe [27]:

$$P = k_{11}T\rho + (k_{02} + k_{12}T + k_{22}T^2)\rho^2 + (k_{03} + k_{13}T + k_{23}T^2)\rho^3 + k_{04}\rho^4 + k_{05}\rho^5 \tag{3}$$

where values of $k_{ij}$ parameters are given in Table 2. The values are based upon the use of a coherent system of SI units (MPa for pressure, kg/L for density, K for temperature).

We have directly calculated $\rho_{\mathrm{vap}}$ by simply counting number of particles inside the cavity and dividing it to the cavity volume. By evaluating $\rho_{\mathrm{vap}}$ of the cavity and using the equation of state, $P_{\mathrm{vap}}$ can be calculated. The results are shown in Fig. 2 for the two isotherms.