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Research paper

Size-effects on the surface tension near the critical point: Monte Carlo simulations of the Lennard-Jones fluid

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ABSTRACT

We report Monte Carlo (MC) simulations of the Lennard-Jones (LJ) fluid at the liquid-vapor interface in the critical region. A slab-based tail method is associated with the MC simulations to approach as close as possible the critical point ($T^* = 0.98T_C^*$). We investigate then the impact of system-sizes on the surface tension and coexisting densities by considering very large box dimensions for which the surface tension is independent of system-sizes at low temperatures.

1. Introduction

Most of the phenomena in surface science adhesion, wetting, lubrication [1,2], nucleation [3,4] involve the combination of liquid-liquid, liquid-vapor, and liquid-solid interfaces. An understanding and control of the surface tension is at the heart of many important industrial and practical processes. The molecular simulations have been extensively used this last decade [5] to reproduce the interfacial tension at different thermodynamic conditions and to describe the interface region in terms of specific arrangements [6,2].

Since 1974 and so far, the calculation of the surface tension from two-phase simulations has been an area of active research. This long-standing activity is explained by the fact that a number of factors such as the surface area (See Fig. 1a and b) [7–12], the cutoff radius and the corresponding long-range corrections [13–20], the truncation of the potential and the force as well as the method used for the calculation of the surface tension [21–27] make the simulated properties dependent on initial conditions. All these issues have been addressed in a recent review [5]. A number of recommendations have been proposed to resolve these issues leading now to an accurate calculation of the surface tension for reduced temperatures less than 0.85 T_C^*.

For higher temperatures, the situation is far from being identical. Indeed, the cutoff-dependence on the surface tension and coexisting densities is still stronger [28]. Recently, we have shown that it is possible to approach the gas-liquid critical point of the Lennard-Jones fluid by performing two-phase simulations of a slab geometry. These simulations have used a slab-based tail [17] methodology with large cutoff values. The main conclusions of this work are that Monte Carlo simulations with the addition of long-range corrections to the energy during the course of the simulations using a reduced cutoff of $r_c^* = 6.4$ reproduce quantitatively the dependencies of the densities and surface tensions on the temperature close to the critical point. In the case of the modeling of methane, the real value of the cutoff corresponds to $r_c = 6.4\sigma = 24$ Å which is twice that used in most atomistic simulations [6,26].

Whereas a reduced cutoff of $r_c^* = 3.0$ is large enough to avoid any cutoff-dependence of the surface tension with a slab-based tail method for temperatures far from the critical point (see Ref. [12]), an increase to $r_c^* = 6.4$ is required to provide reliable surface tensions and coexisting densities in the critical region [28]. A key question arises now: for this large cutoff value of $r_c^* = 6.4$, how do the size-effects affect the values of surface tension and coexisting densities of the critical region? The size-effects will be evaluated trough the variations of the interfacial area $A = L_x \times L_y$ and the longitudinal dimension L_z where z represents the direction normal to the interface. It has been established, at relatively low temperatures, that the size-effects led to oscillatory behaviors of the surface tension with the surface area (Fig. 1a) and the L_z^* dimension (Fig. 1b).

To address this issue, we propose here to investigate LJ liquid-vapor systems close to the critical point with large surface areas and longitudinal dimensions. Fig. 1a and b show the values of sur-

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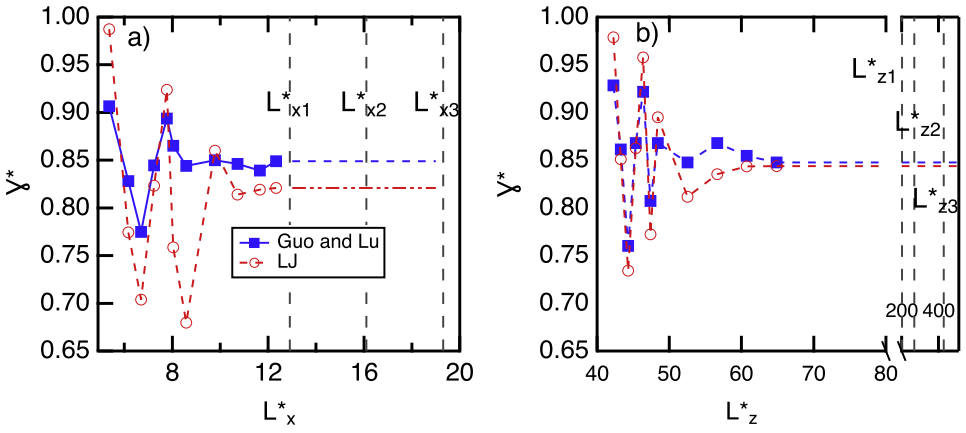

Fig. 1. Surface tensions [10] calculated with the truncated LJ potential and the LJ potential modified with the Guo and Lu slab-based tail methodology at $T^* = 0.8$ for (a) different interfacial areas and (b) L_z^* dimensions. The dotted vertical lines represent the values of interfacial area and of longitudinal dimensions L_z^* investigated here.

face areas $(L_{x1}^*, L_{x2}^*, L_{x3}^*)$ and longitudinal dimensions $(L_{z1}^*, L_{z2}^*, L_{z3}^*)$ considered here. The details of the simulation in terms of box sizes and number of LJ particles are given in Table 1.

2. Methodology

All the properties reported here refer to the Lennard-Jones (LJ) particle and are expressed in reduced LJ units where $T^* = k_B T/\epsilon, \gamma^* = \gamma\sigma^2/\epsilon, L^* = L/\sigma, p^* = p\sigma^3/\epsilon, \quad \rho^* = \rho\sigma^3$ where $T^*, \gamma^*, L^*, p^*, \rho^*$ represent the reduced temperature, surface tension, length, pressure and density, respectively. MC simulations were performed in the constant-*NVT* ensemble. All simulations were organized in cycles. Each cycle consisted of N translations. The equilibration phase was composed of 500 000 cycles and the production phase of 2×10^6 cycles up to 5×10^{10} translation moves. The maximum displacement which was adjusted during the equilibrium phase to give an acceptance ratio of 0.4, was found to be close to 0.23 at $T^* = 1.26$ and to 0.26 at $T^* = 1.28$ in reduced LJ units. The thermodynamic and mechanical properties were calculated every 20 cycles requiring the storage of 100 000 configurations. The statistical errors for these properties were estimated using 5 superblocks averages of 20 000 configurations. The MC calculations were carried out at two reduced temperatures $T^* = 1.26$ and 1.28 for a cutoff radius $r_c^* = 6.4$.

In the Janeček approach, the long-range correction to the truncated potential is added to the truncated $u_{ST}(r_{ij})$ potential. Considering a system of N atoms, the total configurational energy U_{TOT} is

$$U_{TOT} = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} u_{ST}(r_{ij}) + U_{LRC} \tag{1}$$

where r_{ij} is the pair separation distance and $u_{ST}(r_{ij})$ is the spherically-truncated Lennard-Jones potential defined by

$$u_{ST}(r_{ij}) = \begin{cases} u_{LJ}(r_{ij}) & r_{ij} < r_c \\ 0 & r_{ij} \geqslant r_c. \end{cases} \tag{2}$$

u_{LJ} is the Lennard-Jones (LJ) potential defined by ϵ and σ corresponding to energy and size parameters, respectively. The simulation box is divided into N_s slabs of width $\Delta z = 0.13$ (in LJ units). Each slab, which is parallel to the interface, has a volume $V_s = L_x L_y \Delta z$ and z_k defines the centre of the kth slab. In Eq. (1), U_{LRC} is defined as

$$U_{LRC} = \frac{1}{2}\sum_{k=1}^{N_s} u_{lrc}(z_k) \tag{3}$$

where the long-range correction energy of the slab k is

$$u_{lrc}(z_k) = \rho(z_k) V_s \sum_{j=1}^{N_s} \rho(z_j) w(|z_j - z_k|)\Delta z \tag{4}$$

where the sum is over all the slabs in the box. $\rho(z_k)$ defines the density number of the slab k. The contribution $w(\xi) = w(|z_j - z_k|)$is calculated by assuming a uniform distribution of atoms in the slab. For the Lennard-Jones potential, the function $w(\xi)$ is

Table 1
Reduced surface tensions of the LJ fluid calculated at different surface areas A and L_z^* dimensions where N represents the total number of particles in the box. The different contributions of the surface tension, *i.e.*, intrinsic, long range and total parts are given in LJ reduced units. $< \gamma >$ is calculated using the Irving-Kirkwood definition. The subscripts give the accuracy of the last decimal(s), i.e., 0.104_{37} means 0.104 ± 0.037. The surface area A_1 corresponds to 12.9×12.9 and the L_{z1} dimension to 200.9 in reduced units.

$L_x^* \times L_y^*$	L_z^*	N	Box	γ_I^*	γ_{LRC}^*	γ^*
			$T^* = 1.26$			
12.9×12.9	200.9	10796	A_1L_{z1}	0.055_{10}	0.008_1	0.063_{10}
16.1×16.1	200.9	16856	A_2L_{z1}	0.065_7	0.012_1	0.077_7
19.3×19.3	200.9	24259	A_3L_{z1}	0.063_7	0.012_1	0.075_7
12.9×12.9	267.9	16195	A_1L_{z2}	0.083_{20}	0.013_1	0.096_{20}
12.9×12.9	428.6	26992	A_1L_{z3}	0.089_{37}	0.015_1	0.104_{37}
			$T^* = 1.28$			
12.9×12.9	200.9	10796	A_1L_{z1}	0.027_{10}	0.005_1	0.032_{10}
16.1×16.1	200.9	16856	A_2L_{z1}	0.038_{12}	0.010_1	0.048_{12}
19.3×19.3	200.9	10796	A_3L_{z1}	0.038_3	0.006_1	0.045_3
12.9×12.9	267.9	16195	A_1L_{z2}	0.044_{13}	0.008_1	0.052_{13}
12.9×12.9	428.6	26992	A_1L_{z3}	0.061_{13}	0.009_1	0.070_{13}