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INFLUENCE OF THE INTERMOLECULAR INTERACTION POTENTIAL ANISOTROPY ON THE SURFACE TENSION OF MODEL FLUIDS

The thermodynamic and kinetic behavior of liquids even with essentially different types of intermolecular interactions, such as water and argon, exhibits certain similarities. In particular, the kinematic viscosity and the density along the liquid-vapor equilibrium curve in reduced coordinates are similar for those substances. This similarity is explained by the orientation averaging of the intermolecular interaction potential. There arises the question "How universal is the observed regularity?" The aim of this work is to study such thermophysical parameters of a system of diatomic molecules as the surface tension coefficient and the phase densities along the liquid-vapor equilibrium curve, as well as the impact of particle asphericity on these properties. Using the Wang–Landau method in the framework of the grand canonical ensemble, we will calculate the temperature dependences of the densities of the gas and liquid phases at their equilibrium curve, as well as the surface tension coefficient for systems of particles with a non-central interaction. Specifically, the systems of diatomic particles whose atoms interact via the Lennard-Jones potential are examined. The atomic diameters are varied in such a way that the molecular volume remained constant. The influence of the molecular asphericity on the thermophysical properties of the studied liquids are analyzed. It is shown that the anisotropy of the intermolecular interaction potential has almost no effect on the densities of the liquid and gas phases at their equilibrium curve, in contrast to the surface tension coefficient, which substantially depends on the intermolecular interaction potential anisotropy, especially at low temperatures.

Keywords: Wang–Landau method, intermolecular interaction potential anisotropy, surface tension, liquid-vapor equilibrium curve.

1. Introduction

Finding a relation between the parameters of intermolecular interactions and the macroscopic properties of liquids is one of the tasks of the modern statistical physics of liquids. In turn, this domain of science forms a basis for understanding molecular processes that govern a considerable number of surface phenomena, the study of which is the subject of modern molecular physics and non-metallic materials science [1, 2].

One of the fundamental characteristics that govern the course of such processes as the aerosol formation, emulsion stability, wetting, capillary movement, and so forth is the surface tension coefficient. Understanding the indicated processes is of crucial importance, in particular, when developing capillary pumping systems. Capillary pumps use the capillarity effect for passive movement of liquids on the micro- and mesoscopic scales and find their applica-

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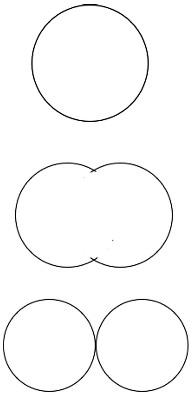

Fig. 1. Models of diatomic molecules with different degrees of non-sphericity, but the same volume: a spherically symmetric molecule ($l/\sigma = 0.0$, top panel), a a non-spherical molecule with $l/\sigma = 0.5$ (middle panel), a non-spherical molecule with $l/\sigma = 1.0$ (bottom panel)

tion in microfluidic devices, electronics cooling systems, biomedical sensors, and so on [3].

The surface tension coefficient is defined as the ratio between a change in the corresponding thermodynamic potential and the change in the interfacial surface area. This parameter is a result of the intermolecular force action, including indirectly through the interface layer structure [4, 5]. The relation between the thermodynamic behavior of the surface tension coefficient and the interaction potential is the subject of intensive research, which is reduced to the analysis of the results of computer simulation of many-particle systems with a given functional dependence of interaction forces on the intermolecular distance and the relative orientation of the molecules [6].

One of the common approaches to such a simulation consists in the adjustment (fitting) of the model potential parameters by comparing the contact angle of a nanodroplet, which is calculated using molecular dynamics simulations, and the "macroscopic" angle measured experimentally [7]. However, this procedure is affected by various factors that violate the isotropy and homogeneity of the system, such as the contact angle hysteresis [8], surface nanotexturing [9], adsorption and selection of the "interface" [10], and the size dependence of surface tension [11], which can differ for bubbles and drops. All those factors can give rise to considerable errors, if the attention is focused only on the "average" contact angle considerring the structural and thermodynamic features of nanodroplets. Therefore, the issues concerning the way through which the potential anisotropy affects the interfacial energy and the significance of the role of the molecular "shape" in comparison with other accompanying effects become even more challenging.

The researchers attempt to study the influence of the features of a particular potential model on the calculation results [12, 13]. In particular, these are the influence of long-range correction [14], the choice of the truncation radius [15], the presence of triple interactions, and others. For instance, the influence of the molecular "shape" or the anisotropy of the interaction potential between the molecules is studied. Namely, the surface tension coefficient is calculated for the systems of particles each of which consists of two force centers ("atoms") located at a certain fixed distance from each other [16]. Different distances between the atoms in such diatomic particles result in their different shapes. However, no attention was paid to the fact that, with such a change of the particle's shape, the particle's own volume also varies.

The purpose of this work is to clarify the "pure" effect of molecular shape on the surface tension coefficient. The idea arose under the influence, on the one hand, of the works, where the influence of the molecular shape on various thermophysical properties of bulk liquids was analyzed [17] and, on the other hand, of the works, where a certain similarity of the thermodynamic behavior of liquids with essentially different nature of intermolecular interaction – for example, water and argon – was detected [18–20]. In particular, the kinematic viscosities and the densities of the indicated substances along the liquid-vapor equilibrium curve are close in reduced coordinates. This similarity is explained by the effect of the interparticle interaction potential averaging over the orientation of molecules. In our opinion, the comparison of the averaged anisotropic potential and the corresponding isotropic potential makes sense if the molecules have identical volumes.

2. Model of Intermolecular Interaction Potential

We chose diatomic molecules (see Fig. 1) as a model of liquid molecules. The potential of interaction between the atoms in them was described by the fourfold-reduced Lennard-Jones potential

$$\phi(r) = \epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right], \tag{1}$$

where σ is the effective diameter of the atom, ϵ is an energy parameter, and r is the distance between the centers of interacting atoms.

The distance l between the atoms in a molecule was rigidly fixed and taken equal to 0, 0.419σ, or 0.794σ. The parameter ϵ was the same in all cases, so that when passing to spherically symmetric molecules ($l = 0$), the interaction potential between such molecules (it is equal to the sum of four atomic potentials) was equal to the Lennard-Jones potential. The parameters σ and l were chosen so that the "volume" of a diatomic molecule was equal to the "volume" of a monoatomic liquid molecule of the first type. Such a choice of the atom-atom interaction potential parameters allowed us, in our opinion, to correctly determine the influence of the interaction potential anisotropy.

3. Method of Calculation of the Surface Tension Coefficient and the Densities of the Liquid and Gaseous Phases on the Equilibrium Curve

The vast majority of studies concerning thermophysical phenomena occurring at the liquid-vapor or liquid-liquid interface are performed using the molecular dynamics method, which is due to the availability of software packages such as LAMMPS and Gromacs. During such a computer experiment, it is necessary to create an interface between homogeneous media. As a result, the number of particles in the main cell can reach tens and hundreds of thousands. Together with the large existence times of metastable states, this circumstance leads to the necessity of applying high-power computer resources.

An alternative approach is the determination of the surface tension coefficient as the difference between the free energies of the gaseous and liquid phases using the Monte Carlo method. Those quantities can be determined through the distribution function of particles over the system. The standard Monte Carlo method does not allow this to be done because of the large difference between the probabilities of the most and least probable states [21]. To overcome this difficulty, several methods have been developed, including the Wang–Landau one [22, 23].

In this work, the surface tension coefficient and the densities of the liquid and gaseous phases on the equilibrium curve were determined using the Wang–Landau method in the framework of the grand canonical ensemble. The corresponding calculations were performed using dimensionless variables. The diameter of hard sphere σ was taken as the length unit, the particle mass m as the mass unit, and ϵ as the energy unit. The normalized density ρ^*, temperature T^*, and surface tension coefficient γ^* in terms of those units are as follows:

$$\rho^* = \frac{N\sigma^3}{V}, \quad T^* = \frac{k_\mathrm{B}T}{\epsilon}, \quad \gamma^* = \frac{\gamma\sigma^2}{\epsilon}, \tag{2}$$

where k_B is the Boltzmann constant, V is the cell volume, and N is the number of particles. The calculations were performed for the reduced temperatures $T^* = 0.90$; 0.95; 1.00; 1.05; and 1.10, which cover most of the equilibrium curve.

For the simulation, four generation types of new configurations were used: the displacement of a random particle as a whole, the addition and annihilation of a particle, and the rotation of a particle by a random angle around its center of mass. The maximum rotation angle and the maximum displacement were chosen so that the corresponding fraction of accepted configurations was 30%. The radius of the atom-atom potential the cut-off was selected to be 2.5σ. The visitation histogram was considered uniform if the number of visits to a state with a certain value of N did not exceed 80% of the average visitation for other states [23]. The initial value of the free energy update factor f was 1. After every cycle, a uniform visitation histogram was achieved; as a result, the latter was zeroed, and the factor f was put equal to one-half of the previous value. This process was repeated until the factor f reached a limit value of 10^{-4}. For generating random numbers, the Mersenne vortex algorithm was applied, which is implemented in the <random> library of the C++ programming language.

The region of liquid and vapor coexistence was determined by selecting the appropriate value for the chemical potential, so that the particle distribution function in the system, $p(N)$, had two peaks with identical areas. Then the vapor, ρ_v^*, and liquid, ρ_l^*, densities were determined using the formulas [23]:

$$\rho_v^* = \sum_{N<N_\mathrm{min}} \frac{N}{V} p(N), \quad \rho_l^* = \sum_{N>N_\mathrm{min}} \frac{N}{V} p(N), \tag{3}$$

where N_min is the number of particles at which the distribution function $p(N)$ has a minimum in between two maxima corresponding to the coexisting phases.

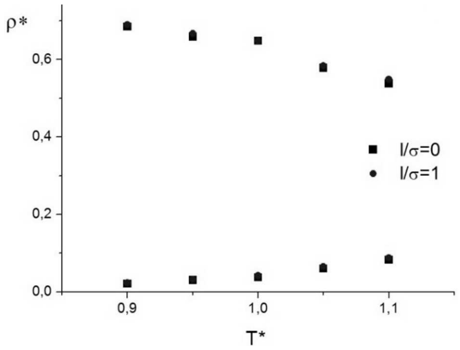

Fig. 2. Dependences of the reduced liquid (upper points) and gas (lower points) densities ρ^* on the reduced temperature T^* for various degrees of the intermolecular interaction potential anisotropy l/σ

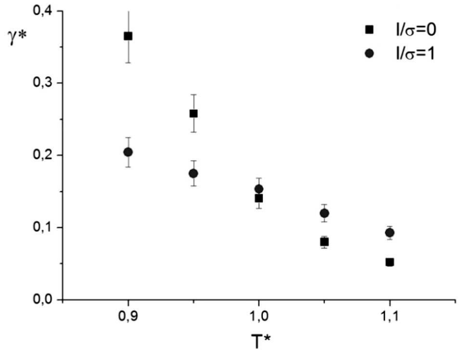

Fig. 3. Dependences of the reduced surface tension coefficient γ^* on the reduced temperature T^* for various degrees of the intermolecular interaction potential anisotropy l/σ. See Fig. 2

The surface tension coefficient was determined by the formula [23]:

$$\gamma^* = \frac{\Delta F}{2L^2}, \tag{4}$$

where L is the cell edge length, and ΔF is the free energy difference between the liquid and gaseous phases. The latter was calculated using the formula

$$\Delta F = \frac{\ln p_l^{\max} + \ln p_v^{\max}}{2} - \ln p^{\min}, \tag{5}$$

where $p_v^{\max}$ and $p_l^{\max}$ are the distribution function values corresponding to the gaseous and liquid phases, respectively, and $p^{\min}$ is the distribution function value at $N = N_{\min}$.

4. Calculation Results

In Fig. 2, the dependences of the reduced liquid and gas phase densities as functions of the reduced temperature are plotted. For the liquid phase, the function $\rho^*(T^*)$ is decreasing and nonlinear. For the gaseous phase, ρ^* increases with the temperature, and its growth rate also increases. This means that the anisotropy of the intermolecular interaction potential has almost no influence on the densities of the liquid and gaseous phases on their equilibrium curve. Therefore, we may assume that, for systems with non-spherical particles, the densities of the liquid and gaseous phases are determined by the averaged interaction potential, and this assumption is consistent with the explanations presented in works [18–20].

In Fig. 3, the dependences of the reduced surface tension coefficient on the reduced temperature for the examined model liquids are shown. As we can see, the values of the surface tension coefficient γ^* decrease with the increasing temperature T^* both for systems with spherically symmetric particles and systems, where the particle shape is not spherical. In the interval of reduced temperatures from 0.9 to 1, 0, the values of the reduced surface tension coefficient for the liquid with non-spherical particles are lower than the corresponding values for the system with spherically symmetric particles. With the increasing temperature, the difference between the surface tension coefficients of the considered liquids becomes insignificant.

5. Conclusions

The temperature dependences of the surface tension coefficient for model liquids with various “non-sphericities” of their molecules can be explained by assuming that, among other factors, these dependences are determined by the presence of short-range orientational order. As the temperature increases, this order is destroyed, which leads to a reduction in the difference between the thermodynamic characteristics of liquids consisting of spherical and non-spherical particles. Thus, the surface tension coefficient, unlike the density, is not the thermodynamic characteristic which behavior for liquids with central and non-central particle interactions is similar. In general, the results of the presented study also testify that the surface tension coefficient is a physical quantity that is sensitive to the details of the intermolecular interaction potential.

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ВПЛИВ АНІЗОТРОПІЇ ПОТЕНЦІАЛУ МІЖМОЛЕКУЛЯРНОЇ ВЗАЄМОДІЇ НА КОЕФІЦІЄНТ ПОВЕРХНЕВОГО НАТЯГУ МОДЕЛЬНИХ ФЛЮЇДІВ

Термодинамічна та кінетична поведінка рідин із суттєво різним характером міжмолекулярної взаємодії, таких як вода та аргон, демонструє певну подібність. Зокрема, кінематична в'язкість та густина на лінії рівноваги рідина–пара у зведених координатах є близькими для аргону та води. Ця подібність пояснюється усередненням за орієнтаціями потенціалу міжмолекулярної взаємодії молекул. Виникає питання, наскільки універсальною є виявлена закономірність. Метою роботи є дослідження таких теплофізичних параметрів системи двоатомних молекул, як коефіцієнт поверхневого натягу та густина на лінії рівноваги рідина–пара, а також вплив несферичності частинок на відповідні властивості. Методом Уанга–Ландау у великому канонічному ансамблі розраховано температурні залежності густини газової та рідинної фази на лінії їх рівноваги та коефіцієнта поверхневого натягу систем частинок з нецентральною взаємодією. А саме, розглянуто системи двоатомних частинок, взаємодія атомів яких описується за допомогою потенціалу Леннарда-Джонса. Діаметр атомів варіювався таким чином, щоб об'єм молекули залишався сталим. Проаналізовано вплив несферичності молекул на теплофізичні властивості дослідженого флюїду. Показано, що анізотропія потенціалу міжмолекулярної взаємодії майже не впливає на густину рідинної та газової фаз на лінії їх рівноваги на відміну від коефіцієнта поверхневого натягу, для якого вплив анізотропії потенціалу міжмолекулярної взаємодії є помітним, особливо при низьких температурах.

Ключові слова: метод Уанга–Ландау, анізотропія потенціалу міжмолекулярної взаємодії, поверхневий натяг, лінія рівноваги рідина–пара.