1. INTRODUCTION

The problem of size dependence of the surface tension of droplets has been discussed as early as by Gibbs [1]. Tolman, based on the developed method of surface phases, derived his known formula [2]

\[ \gamma(R) = \frac{\gamma_{\infty}}{1 + 2\delta/R} \]  

(1)

for the surface tension \( \gamma \) of a droplet with radius \( R \). Here, \( \gamma_{\infty} \) is the asymptotic (macroscopic) value of surface tension corresponding to \( R \rightarrow \infty \) and \( \delta \) is the parameter called the Tolman length. Note that thermodynamic derivation of formula (1) is referred only to the case when \( R \gg \delta \). For small \( R \) values, Rusanov obtained linear dependence [3, 4]

\[ \gamma(R) = KR, \]  

(2)

where \( K \) is the proportionality coefficient dependent on temperature.

The development of nanotechnology [5] promoted a new flash-up of interest in the surface tension of small objects. However, different points of view are often stated concerning the size dependence of surface tension. For example, in experimental work [6], the notion of surface tension was applied to the nuclei of a spherical container studied at constant temperature by the molecular dynamics method. The distribution of local density is found and size dependences of density in the center of droplet, first coordination number, and energy surface tension coinciding for equimolecular dividing surface with specific excess free energy of droplet are studied. Radial distribution function is also determined. It is established that the passage of structural characteristics to their macroscopic values is observed for droplets containing as little as about 300 molecules, while, for energy surface tension, analogous passage for energy surface tension occurs for droplets containing 700–6000 molecules.

Since substantial difficulties arise in the experimental study of structural and thermodynamic characteristics of nanodroplets, methods of numerical simulation, particularly molecular dynamics method, acquire special significance. In the methodological aspect, these methods occupy an intermediate position between theory and experiment. The first molecular dynamics studies of small droplets were performed as early as in the 1970s (see [8]); moreover, one of the pioneers' work in this field of research was carried out by Brodskaya and Rusanov [9, 10]. The complex character of this work should be particularly noted; the authors studied both the structural characteristics of nanodroplets (distributions of density and components of pressure tensor) and size dependences of melting points and surface tension.

Note that, because it is normal for works on numerical simulation [8–11], quasi-hydrostatic definition of surface tension is directly or indirectly used as an integral measure of the deviation of small object from the Pascal law. We believe that the calculation of the components of pressure tensor for objects containing several hundreds or, moreover, dozens of atoms is not quite correct. Naturally, the use of the notion of local density for small objects also involves some difficulties, which, however, are not so crucial. Our point of view can be confirmed by the fact that the characteristic thickness of vapor–liquid interface determined by the density is about a dozen effective molecular diameters, while that determined by the anisotropy of pressure tensor is about 100 diameters [4].

Taking into account the aforementioned, we believe that, as applied to nanoparticles, the energy definition of the surface tension as the formation work of small object per unit area of chosen dividing surface is more
correct. According to Rusanov [12], we will call this parameter the energy surface tension.

2. METHOD OF STUDY

For the simulation of equilibrium configurations of nanodroplets, we used the method of isothermic molecular dynamics. Thermostating was performed by the Berendsen method [13] with the additional control of Maxwell-type distributions of molecules over velocities and so-called “hot points,” which can arise when using the Berendsen thermostat.

The software for the molecular dynamics simulation of the evolution of nanoparticles and, hence, their equilibrium configurations, was developed preliminarily and tested in the problem of the spreading of nanodroplets of simple and polymeric liquids [14–17]. This software also makes it possible to simulate the evolution and equilibrium state of globular nanoparticles placed in a container of arbitrary shape, particularly spherical. The choice of such a shape is the most convenient, since in this case, the least number of molecules is consumed to create the vapor phase which is in equilibrium with the nanoparticle.

The initial configuration of nanodroplet was set as follows. Molecules are randomly placed into a sphere with radius $R_0$ until the preset initial value of reduced density $n^* = na^3$ ($n = N/V$ is the numerical density of molecules and $a$ is their effective diameter) is achieved. In particular, it was assumed that, at reduced temperature $T^* = kT/e = 0.7$ (where $k$ is Boltzmann’s constant and $e$ is the energy parameter of pair potential), which corresponds to the macroscopic melting temperature $T^*$ [18], $n_m^* = 0.9^1$. Created initial configuration was brought to equilibrium in preset initial volume $V_0 = 4/3\pi R_0^3$. After this initial relaxation, the nanoparticle was placed into a spherical container with a slightly larger radius ($R_1 > R_0$). Distance $R_1 − R_0 = 2R_0$ from the surface of initial (unrelaxed) droplet to the walls of container exceeds the radius of pair potential at $R^*_0 = R_0/a > 2$. Repeated relaxation of nanoparticle was performed in container at specified temperature. In the process of relaxation, part of the molecules evaporated to form a vapor that is at equilibrium with nanodroplet. The walls of container softly reflected molecules so that there would be neither additional losses due to adsorption on container walls nor the violation of equilibrium at the elastic reflection of molecules. The final value of radius $R$ of equilibrium nanodroplet was determined after the calculation of local density distribution by the position of equimolecular dividing surface (for more detail, see Section 3). Afterwards, we computed structural and thermodynamic characteristics of the droplet using special programs.

3. RESULTS OF SIMULATION

The simulation was carried out with a fairly small step of reduced time $\Delta t^* = \Delta t/t_0 = 10^{-3}$, where $t_0 = \sqrt{M a^2/N_A \varepsilon}$ is the characteristic time ($M$ is the molecular mass of substance comprising droplet and $N_A$ is Avogadro’s number). For argon, which is more often used as model Lennard-Jones fluid [8–11, 27–30], $t_0 = 2$ ps. Correspondingly, $\Delta t = 2 \times 10^{-3}$ ps that is approximately by an order of magnitude smaller than the value of step $\Delta t = 10^{-2}$ ps used by Brodskaya and Rusanov [9, 10]. The time of relaxation, i.e., the time of the transition of the initial droplet to the equilibrium state was, on average, $2 \times 10^4$ steps. For argon, this number of steps corresponds to a time interval equal to 40 ps. This time exceeds that was reported in [9, 10] (10 ps), but matches this value in its order of magnitude. After the relaxation ended, structural and thermodynamic characteristics of nanodroplets were averaged at the time interval corresponding to $10^4$ steps of evolution.

Figure 1 shows the results of calculations of radial density distribution in nanodroplets with radii that differ approximately twofold at reduced temperature $T^* = 0.7$, which corresponds, according to our previous results [18], to the asymptotic (at large radii) value of the melting temperature of Lennard-Jones particles. If we take advantage of the values of the parameters of Lennard-Jones potential for argon, $\varepsilon/k = 119.8$ K and $a = 0.96$, which satisfactorily agrees with our estimate $n_m^* = 0.8$ based on molecular dynamics experiments.

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1 In accordance with the stability condition for simple fluid proposed by Fisher [19], at the melting temperature, $n_m^* = 3 \pi \varepsilon / k \approx 0.96$, which satisfactorily agrees with our estimate $n_m^* = 0.8$ based on molecular dynamics experiments.