Brief Communications

Comparison of the properties of metastable and equilibrium drops in the vapor phase

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The properties of metastable and equilibrium drops that occur in the vapor phase and differ in the size and position of the dividing surface are compared. Using an equimolecular dividing surface, it was found that the total free energy and the total mass of the substance in drops of the same size over a broad temperature range differ by not more than 0.3%. A similar comparison for a dividing surface chosen from the equality condition of the moments of forces gives rather similar results. Using the surface where the maximum surface tension is attained as the dividing surface is impossible at low temperatures, because under these conditions, the notion of surface tension has no physical meaning. At high temperatures, the difference between the total mass of the substance for metastable and equilibrium drops does not exceed 0.6%. The calculations were carried out over a broad temperature range on the basis of the lattice-gas model in the quasichemical approximation.

Key words: spherical drops, width of interfacial layer, equimolecular surface, surface tension, lattice-gas model, quasichemical approximation.

Thermodynamic properties of drops have been actively used till now to study the dynamics of formation of new phases.[1—4] They are used to calculate the energy of formation of seeds in the studies of the first-order phase transition kinetics. However, transition to molecular models is rather slow.[5—10]

A number of publications[11,12] proposes an approach based on the lattice-gas model.[13,14] Previously, this model has been widely used[6,7,15—18] to calculate planar vapor—liquid interface. By means of molecular theory,[11,12] it was possible to study not only metastable but also equilibrium drops existing at the saturated vapor pressure, which had been scarcely considered before. Detailed analysis of equilibrium drops was published previously.[19]

In this study the following properties are compared for metastable and equilibrium drops of the same size: local densities, pressure, surface tension, total free energy, the total drop mass, and the difference between the chemical potentials inside metastable and equilibrium drops of the same size at a specified temperature.

All equations and calculation methods have been described in detail;[13,14,19] therefore, here we report only the final results.

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The calculation was carried out for a broad range of reduced temperatures $\tau = T/T_c$ (T_c is the critical temperature in the bulk phase) from the triple point ($\tau = 0.55$) to the near-critical region $\tau < 0.9$. The comparison was done using traditional methods for determining the surface tension of metastable drops relative to three types of the dividing surface. These include (a) equimolecular surface, (b) surface chosen from the equality condition of moments of forces, and (c) the dividing surface chosen based on the maximum surface tension. For an equilibrium drop, the surface tension was defined on the equimolecular surface.

Metastable drops have the density θ_1 of the liquid, internal pressure π_1, and the chemical potential μ_1, which differs by $\Delta\mu$ from the chemical potential of the vapor, which has the density θ_κ, pressure π_κ, and the chemical potential μ_κ (see Ref. 11). Here the character κ means the number of a monolayer in the interfacial region corresponding to the vapor. The state of the vapor is unambiguously specified by the system temperature T and the saturation vapor pressure $\pi_0(T)$ at the given temperature, $\pi_\kappa = \pi_0(T)$. The liquid and vapor pressures are related to each other by the Laplace equation: $\pi_1 - \pi_\kappa = 2\sigma/(R + \rho)$, where σ is the surface tension, R is the drop radius, $R + \rho$ is the radius of the dividing surface. The three ways of defining the dividing surface outlined above can be used to calculate σ.

The key feature of an equilibrium drop is that the molecules located inside the drop and in the vapor have the same chemical potential $\mu_1 = \mu_\kappa$ (and $\Delta\mu = 0$) and, as a consequence, the pressures in the vapor and in the drop are equal ($\pi_1 = \pi_\kappa = \pi_0(T)$).

In each phase, the pressure and density inside the drops or in the vapor are unambiguously related to each other by the state equation of the given phase. The liquid density and pressure in a metastable drop are higher than these values for an equilibrium drop.

The effect of the radius R of the liquid part of the drop on the properties of metastable drops is illustrated by Fig. 1. Figure 1, *a* shows the density ratio for the liquid parts of

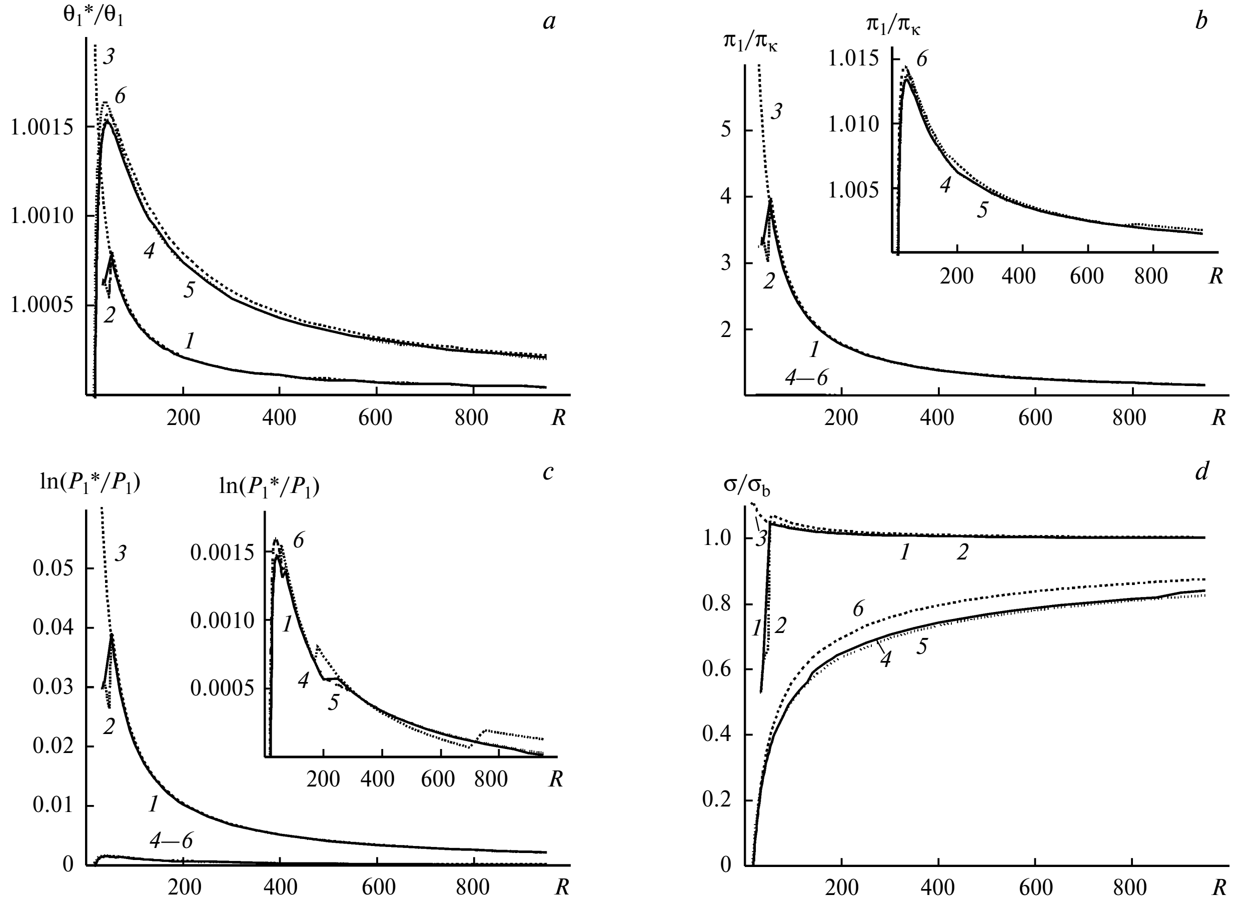

Fig. 1. Effect of the radius R on the density ratio of the liquid parts of metastable and equilibrium drops $\theta^*{}_1/\theta_1$ (*a*), ratio of their inner pressures in the liquid $\pi^*{}_1/\pi_1$ (*b*), difference of these pressures (*c*), and relative surface tension σ/σ_b (*d*). The results are given for $\tau = 0.55$ (*1—3*) and 0.89 (*4—6*) for three definitions of the dividing surface: equimolecular surface (*1*, *4*), surface based on the balance of moments of forces (*2*, *5*), and tension surface (*3*, *6*). The drop radii (R) were measured in terms of the lattice structure parameter numbers λ related to the Lennard-Jones potential parameter: $\lambda = 1.12\ \varepsilon$.

metastable and equilibrium drops, Fig. 1, *b* shows the ratio of their internal pressures in the liquid, and Fig. 1, *c* presents the chemical potential difference $\Delta\mu = \mu_1 - \mu_\kappa$ at the dividing surface ρ of a metastable drop ($\mu = \ln P$). Finally, Fig. 1, *d* presents the relative surface tension σ/σ_b. Here $\sigma_b = \sigma_\infty$ is the surface tension for $R \to \infty$ or, what is the same, for a planar lattice.

The curves in Figs 1, *a—c* have the same form for the equimolecular surface and the surface corresponding to equal moments of forces: as the radius decreases, the considered parameter first increases to some maximum value and then decreases to zero. For very small sizes, all curves that refer to metastable drops coincide with the corresponding curves for equilibrium drops. This general trend does not rule out local jumps at low temperatures and small radii. These jumps may be caused by the discrete nature of the calculation model.[11] However, the general pattern of variation of characteristics demonstrating the presence of maximum supersaturation is retained.

Figure 2 shows the logarithmic dependences of the total energy ratios for metastable and equilibrium drops of equal size (*a*) and the ratios of the masses of the same drops (*b*) on their size *R*. The subscript indicates the type of drop.

Due to inhomogeneity of a drop, its mass *m* is defined as the product of local densities by local volumes of different areas of the drop $m = V_l\theta_l + \Sigma_{q=2}{}^{\kappa-1}4\pi(R + \rho)^2\theta_q$, where the drop volume $V = V_l + V_\kappa$ consists of the liquid volume $V_l = 4\pi R_l{}^3/3$ and the volume of the liquid to vapor transition layer with the width κ ($V_\kappa = \Sigma_{q=2}{}^{\kappa-1}4\pi(R + \rho)^2$), where *q* is the number of the layer of the transition region ($2 \le q \le \kappa - 1$). The value $q = 1$ refers to the liquid part of the drop and $q = \kappa$ corresponds to the vapor phase.

The total free energy of a drop is expressed as $E = V_lE_l + \Sigma_{q=2}{}^{\kappa-1}4\pi(R + \rho)^2E_q$, where E_l is the free energy inside the drop per unit of the liquid; E_q is a similar value for a unit in layer *q* in the liquid to vapor transition region.

The calculations in terms of the molecular model of a spherical drop located in the vapor phase showed rather similar values for the inner properties of metastable drops of different size for all three traditional methods of calculation of the properties of a metastable drop differing in the position of the dividing surface (equimolecular surface, equality condition for the moments of forces, and at the tension surface).

The following values are significant: the difference between the total free energies of the metastable and equilibrium drops and the difference between the total substance mass contained in these drops. The calculation showed that for the use of equimolecular dividing surface and the surface chosen from the equality condition of the moments of forces, these values differ by nore more than 0.3% over a broad temperature range from the triple point to the near-critical region.

In a comparison of equilibrium drops confined by an equimolecular surface with a metastable drop confined by a tension surface, this difference at high temperature does not exceed 0.6%. At low temperatures ($\tau < 0.7$), this comparison is impossible due to the absence of a tension surface in the metastable drop, which also implies the absence of maximum supersaturation.[11,19] The absence of the proper notion of the tension surface and of maximum supersaturation at low temperatures indicates that the conditions of thermodynamic constructions are not fulfilled at any parameters of the state of the system.

The minor differences between the total free energies and the total substance masses of metastable and equilibrium drops of the same size indicate that modern experimental methods do not make it possible to distinguish between the contributions of these two types of drops to the system thermodynamic parameters. In addition, the presence of drops that may exist in different thermodynamic states in the system requires using more advanced

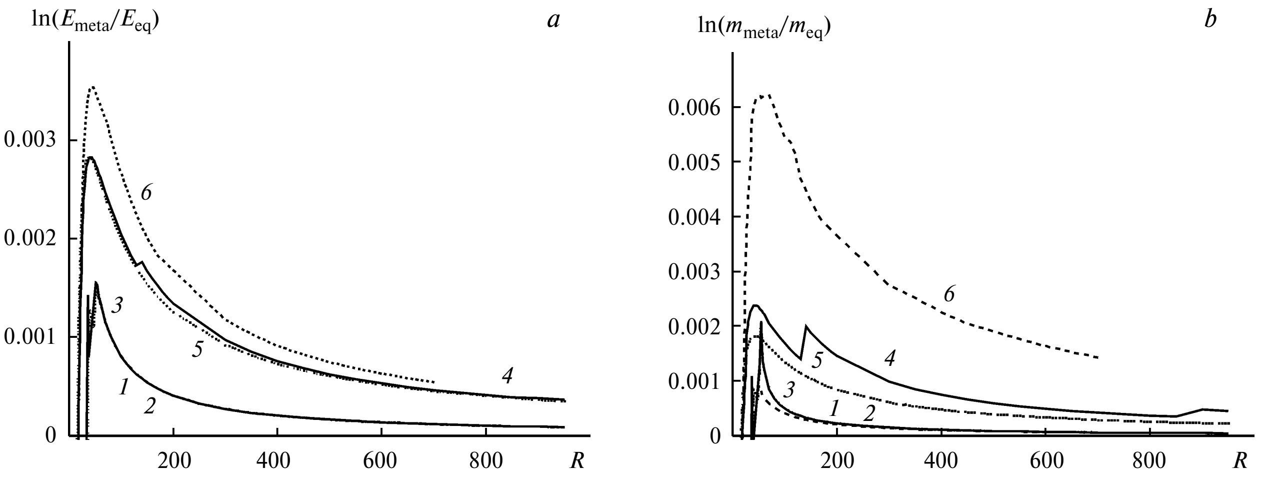

Fig. 2. Relative difference for the metastable and equilibrium drops *vs.* their radius *R* for $\tau = 0.55$ и 0.89: total free energy E_{meta}/E_{eq} (*a*) and drop mass m_{meta}/m_{eq} (*b*). For curve designations, see Fig. 1.

kinetic models than the transitional approaches taking into account only metastable drops for describing the condensation process.[1—4] The existence of equilibrium drops[11,19] attests to inadequacy of the thermodynamic description of the vapor condensation process.

References

1. J. W. Gibbs, *Thermodynamics. Statistical Mechanics*, Nauka, Moscow, 1982, 584 pp. (Russian Translation).
2. M. Volmer, *Kinetik der Phasenbildung*, Verlag Von Theodor Steinkopff, Drezden—Leipzig, 1939.
3. Ya. I. Frenkel´, *Kineticheskaya teoriya zhidkostei* [*Kinetic Theory of Liquids*], Izd. AN SSSR, Moscow—Leningrad, 1945, 592 pp. (in Russian).
4. A. I. Rusanov, *Fazovye ravnovesiya i poverkhnostnye yavleniya* [*Phase Equilibria and Surface Phenomena*], Khimiya, Leningrad, 1967, 322 pp. (in Russian).
5. F. P. Buff, J. G. Kirkwood, *J. Chem. Phys.*, 1950, **18**, 991.
6. S. Ono, S. Kondo, *Molecular Theory of Surface Tension in Liquids*, Springer—Verlag, Berlin—Göttingen—Heidelberg, 1960.
7. J. S. Rowlinson, B. Widom, *Molecular Theory of Capillarity*, Clarendon Press, Oxford, 1982.
8. C. A. Croxton, *Liquid State Physics — A Statistical Mechanical Introduction*, Cambridge University Press, Cambridge, 1974.
9. M. Iwamatsu, *J. Phys.: Condens. Matter.*, 1994, **6**, L173.
10. V. G. Baidakov, G. Sh. Boltachev, *Zh. Fiz. Khim.*, 1995, **69**, 515 [*Russ. J. Phys. Chem.* (*Engl. Transl.*), 1995, **69**].
11. Yu. K. Tovbin, A. B. Rabinovich, *Izv. Akad. Nauk, Ser. Khim.*, 2009, 2127 [*Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 2193].
12. Yu. K. Tovbin, *Zh. Fiz. Khim.*, 2010, **84**, 231 [*Russ. J. Phys. Chem.* (*Engl. Transl.*), 2010, **84**, No. 2].
13. Yu. K. Tovbin, *Theory of Physical Chemistry Processes at a Gas—Solid Interface*, CRC Press, Boca Raton, 1991.
14. T. L. Hill, *Statistical Mechanics. Principles and Selected Applications*, McGraw—Hill Book Comp. Inc., New York, 1956.
15. I. Prigogine, R. Defay, *J. Chim. Phys.*, 1949, **46**, 367.
16. R. Defay, I. Prigogine, A. Bellemans, D. H. Everett, *Surface Tension and Adsorption*, Longmans, Green and Co., London, 1966.
17. A. W. Adamson, *Physical Chemistry of Surfaces,* 3rd ed., Wiley, New York—London—Sydney—Toronto, 1975.
18. N. A. Smirnova, *Molekulyarnye teorii rastvorov* [*Molecular Theories of Solutions*], Khimiya, Leningrad, 1987, 334 pp. (in Russian).
19. Yu. K. Tovbin, A. B. Rabinovich, *Izv. Akad. Nauk. Ser. Khim.*, 2010, 663 [*Russ. Chem. Bull., Int. Ed.*, 2010, **59**, No. 4].

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