Curvature effect on the physical boundary of metastable states in liquids

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Abstract

The physical boundary of metastable states, the kinetic spinodal, is introduced as a locus where the lifetime of metastable state becomes shorter than a relaxation time to local equilibrium. The theory does not contain any adjustable parameters. If the surface tension is known, the kinetic spinodal is completely determined by the equation of state only. The curvature effect on the surface tension and nucleation barrier is considered and a general, curvature-corrected, equation for the kinetic spinodal is developed. The theory was tested against experimental data for the homogeneous nucleation limit of superheated, stretched, and supercooled water. In all cases, good agreement between theoretical predictions and experimental data was achieved. We find that in water, the Tolman length is negative and the curvature effect increases the surface tension and the nucleation barrier. The glass transition in supercooled water is also discussed. The high-temperature limit for glassy states is introduced as a second root of the kinetic equation in supercooled fluids. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Curvature effect; Glass transition; Homogeneous nucleation; Kinetic spinodal; Metastable water; Surface tension

1. Introduction

In the thermodynamic theory of phase transitions, the locus of states of infinite compressibility, the spinodal, is considered as a boundary of fluid metastable states [1]. Physically, however the metastable state becomes short-lived well before the spinodal is reached [2,3]. In the fluctuation theory of relaxation of metastable states developed by Patashinskii and Shumilo [4,5], the physical boundary of metastable states, the kinetic

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spinodal, is determined as a locus where the mean-time of formation of a critical nucleus of stable phase, t_M, becomes shorter than a characteristic time governing the decay of fluctuations to local equilibrium, t_R. Both times, t_M and t_R, depend on the kinetic properties of the liquid, but the ratio t_M/t_R depends on the thermodynamic properties only. Therefore, the physical boundary of metastable states in this approach is completely determined by the equilibrium properties of the system.

In the present work, we continue the study of the kinetic boundary of metastable states initiated in our previous works [6–9]. Here we introduce a curvature effect on the surface tension into nucleation theory and consider the kinetic boundary of metastable states in superheated, stretched, and supercooled water.

2. Theoretical background

The dynamics of a system in a metastable state of the initial phase is connected with the relaxation and fluctuations of the hydrodynamic fields of the order parameter $\varphi(\vec{x}, t)$ [4,5]. The slowness of its relaxation allows excluding other degrees of freedom and consideration of the dynamics of the order parameter only. In this case, the equation of motion of the system is [10]

$$\frac{\partial \varphi}{\partial t} = -\Gamma_c \Delta \left(\frac{\partial H}{\partial \varphi} + f_{st} \right) \tag{1}$$

where Γ_c is a transport coefficient, H is an effective Hamiltonian, and f_{st} is an external random force modeling thermal fluctuations. Near the stability region, the effective Hamiltonian can be represented in the form [5]

$$H\{\varphi\} = \int d^3 r \left(\frac{g}{2} (\nabla \varphi)^2 + \frac{u_2}{2} \varphi^2 + \frac{u_3}{3} \varphi^3 \right) , \tag{2}$$

where $g, u_2, u_3 > 0$, and u_2 are assumed to be small. The curve $u_2 = 0$ represents a bare or "unrenormalized" spinodal (i.e., a spinodal of the system in the absence of fluctuations). The solution of Eqs. (1) and (2), which was obtained by Patashinskii and Shumilo [4,5] yields a lifetime of the metastable phase, which accounts for fluctuations and is given by

$$t_M = t_R \left(\frac{4\pi\gamma}{\lambda_0} \right) \exp(\gamma W_{\min}/k_B T) . \tag{3}$$

In this equation $t_R = 16g/\Gamma_c u_2^2$ is a characteristic time governing the relaxation toward local equilibrium, $W_{\min}$ is the nucleation barrier, which is equal to the minimum reversible work required to form a critical size nuclei, the dimensionless parameter $\gamma = (u_2 g)^{3/2}/k_B T u_3^2$, and $\lambda_0 \cong 8.25$ is a dimensionless constant. When $\gamma W_{\min} \gg k_B T$, the lifetime of the metastable phase is much longer than the relaxation time t_R, and the metastable state is statistically well defined. For $\gamma < k_B T/W_{\min}$, the initial homogeneous state, as a result of fluctuations, transforms to a heterogeneous state during a time comparable with the time governing the relaxation toward local equilibrium ($t_M \cong t_R$).

The curve $\gamma W_{\min} = k_B T$, or, alternatively,

$$u_2 = (u_2)_{KS} = \frac{1}{g} \left[\frac{(k_B T u_3)^2}{W_{\min}} \right]^{2/3} , \tag{4}$$

can be regarded as the physical (kinetic) spinodal, which limits the region in the phase diagram $(u_2 > (u_2)_{KS})$ of statistically well defined and experimentally attainable metastable states. For $0 < u_2 < (u_2)_{KS}$ the lifetime $t_M < t_R$ and the very concept of an equilibrium homogeneous state is no longer applicable, and this spinodal region separates metastable and unstable states in the phase diagram of the system.

As was shown by Kiselev [8,11], in one-component fluids the parameters u_2 and u_3 are directly related to the first and second derivatives of the chemical potential, μ, with respect to the density

$$u_2 = \rho \left(\frac{\partial \mu}{\partial \rho} \right)_T = k_B T \rho \bar{\mu}_\rho, \quad u_3 = \frac{1}{2} \rho^3 \left(\frac{\partial^2 \mu}{\partial \rho^2} \right)_T = \frac{1}{2} k_B T \rho \bar{\mu}_{\rho\rho} \tag{5}$$

and for the parameter g a good estimate is

$$g = k_B T (\rho^*)^{1/3} \tag{6}$$

where ρ^* is a characteristic density in the system. Eq. (4) for the kinetic spinodal, using Eqs. (5) and (6), can be written in the form

$$\bar{\mu}_\rho(T_{KS}) = \left[\frac{k_B T \bar{\mu}_{\rho\rho}^2(T_{KS})}{4 W_{\min}(T_{KS})} \right]^{2/3} \left(\frac{\rho}{\rho^*} \right)^{1/3} , \tag{7}$$

where for the characteristic density in the superheated and stretched liquids, one can use the critical density, $\rho^* = \rho_c$ [6–8], while in supercooled liquids one can set ρ^* equal to the density of liquid in the triple point, $\rho^* = \rho_{tr}$ [11]. If an explicit expression for the nucleation barrier $W_{\min}(T)$ is known, the temperature T_{KS} at the kinetic spinodal can be found from a solution of Eq. (7).

3. Nucleation barrier

A general thermodynamic expression for the nucleation barrier for a spherical nucleus with the radius r in the bulk liquid phase can be written in the form [8]

$$W_{\min}(r) = \frac{4}{3} \pi r^3 \frac{\mu_N(P_N) - \mu_L(P)}{v_N} + \frac{4}{3} \pi r^2 \sigma , \tag{8}$$

where the subscripts "N" and "L" correspond to the nucleus and the bulk liquid phase, respectively, v_N is the molar volume, $P_N = P + \sigma/2r$ is the pressure in the nucleus, and σ is the surface tension. The critical radius of the nucleus, r_c, is determined from the condition

$$\left(\frac{\partial W_{\min}}{\partial r} \right)_{P,T} = 0 \tag{9}$$

which for the surface tension dependent on the radius of the nucleus r is equivalent to

$$\mu_N(P_N) = \mu_L(P) - v_N \left(\frac{\partial \sigma}{\partial r} \right)_T . \tag{10}$$

For the curvature-independent surface tension $\sigma = \sigma_0(T)$, Eq. (10) takes a simple form

$$\mu_N(P_N) = \mu_L(P) , \tag{11}$$

where $P_N = P + \sigma/2r_c^0$. For the spherical vapor nucleus in the metastable liquid, a good approximation for the solution of Eq. (11) is [8]

$$r_c^0 = \frac{2\sigma_0^{VL}}{P^*} \left[\exp\left(\frac{v_L^*(P - P^*)}{k_B T} \right) - \frac{P}{P^*} \right]^{-1} , \tag{12}$$

while for the spherical crystal nucleus in the supercooled liquid the critical radius is given by [2,3]

$$r_c^0 = \frac{T_m(P)\sigma_0^{SL}(T)v_S^*(T)}{\Delta h \Delta T} . \tag{13}$$

In Eqs. (12) and (13) σ_0^{VL} and σ_0^{SL} are the surface tension at the planar vapor–liquid and solid–liquid interfaces, respectively, Δh is the molar enthalpy of fusion, T_m is a melting temperature at given pressure P, and $\Delta T = T_m - T$ is a degree of supercooling, and the superscript "*" denotes the properties on the coexistence curve.

In general, the surface tension is a function of the radius of the curvature r [12–16]. Here we focus in particular curvature correction defined by the Tolman length δ_T [17]

$$\sigma = \sigma_0(T) \left(1 - 2\frac{\delta_T}{r} \right) . \tag{14}$$

A solution of the Eq. (10) for the critical radius of the nucleus with the surface tension as given by Eq. (14) can be written in the form

$$r_c = \frac{1}{2}r_c^0 \left(1 + \sqrt{1 - 4\frac{\delta_T}{r_c^0}} \right) , \tag{15}$$

where r_c^0 is the critical radius of the nucleus introduced above (see Eqs. (12) and (13)). Eq. (8) for the nucleation barrier in this case reads

$$W_{\min} = \frac{4}{3}\pi r_c^2 \sigma_0(T) \left(1 - 4\frac{\delta_T}{r_c} \right) . \tag{16}$$

4. Comparison with experimental data

In order to calculate the kinetic spinodal using Eq. (7), one needs to know the equation of state, which can be extrapolated into the metastable region, the surface tension of the plane interface $\sigma_0(T)$, and the Tolman length δ_T. For a comparison of the theory with experimental data, we consider here metastable water, for which all of these properties were studied in detail.
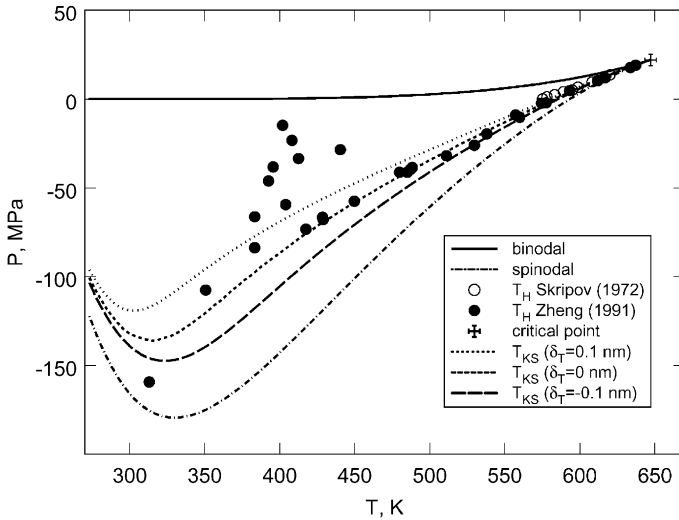
Fig. 1. *P–T* diagram of superheated and stretched water. The solid line represents the coexistence curve, the symbols correspond to the homogeneous nucleation, T_H, obtained by Skripov [2] (open circles) and by Zheng [20] (filled circles), the dotted, short-dashed, and long-dashed lines represent the kinetic spinodal, T_{KS}, calculated with the Tolman length $\delta_T = 0.1$, 0, and -0.1 nm, respectively, and the dashed-dotted curve represents the spinodal.

Firstly, we apply the theory to calculation of the kinetic spinodal in superheated and stretched water, which was considered before by Kiselev et al. [7,8] with the assumption that $\delta_T = 0$. In this work, we calculate the kinetic spinodal in superheated and stretched water with $\delta_T = 0.1$ nm obtained by Tolman [17] for the water droplets at $T = 293$ K. For the surface tension at the plane vapor–liquid interface, $\sigma_0^{VL}(T)$, we adopted the equation of Vargaftik et al. [18], and for the representation of the thermodynamic properties of metastable water we used the IAPWS-95 formulation [19]. Our results are compared with earlier results in Fig. 1. The previous results shown in Fig. 1 are those of Kiselev et al. [7,8], experimental data for the nucleation limit obtained by Skripov [2] and values recalculated into the *P–T* plane by Zheng [20]. As one can see, in the critical region, at $575 \text{ K} \leqslant T \leqslant T_c$, the curvature effect on the kinetic spinodal is small and both curves with $\delta_T = 0$ and $\delta_T = 0.1$ nm practically coincide. In both cases, excellent agreement with experimental data is observed. However, in the low temperature region, at $T \leqslant 550$ K, the curvature effect becomes essential.

The kinetic spinodal calculated with the positive value of the Tolman length (dotted curve in Fig. 1) lies above the homogeneous nucleation temperatures, a result that is physically incorrect. A much better result is achieved with a negative value of the Tolman length, $\delta_T = -0.1$ nm, (long-dashed curve in Fig. 1). This result is clearer in Fig. 2, where the original data obtained by Zheng [20] are shown. Thus, with the IAPWS-95 formulation [19] for water and steam, we obtain negative values for the Tolman length. It is interesting to note that the negative value of the Tolman
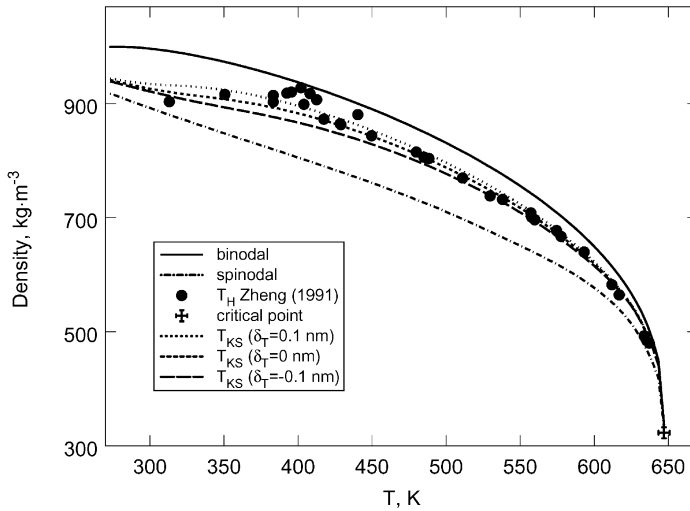
Fig. 2. ρ–T diagram of superheated and stretched water. The legend as in Fig. 1.

length, $\delta_T < 0$, has been also obtained earlier by Zhukovitskii [15] from his independent analysis of the size-corrected effect on homogeneous nucleation in water but we also note that Ref. [16] argued that $\delta_T > 0$. Since water is a complex fluid with different anomalous properties [21], we cannot say for sure if the negative length result is really correct or if it is arising from an "illegal" extrapolation of the empirical formulation [19] into the region where no experimental data were used.

We have also compared the theory with experimental data obtained by Angell and coworkers for supercooled water [22,23]. In supercooled liquids, the situation in general is more complicated than in superheated liquids. The primary reason for this is that an equation of state obtained from the analysis of experimental data for the stable liquid, as a rule, cannot be extrapolated into the supercooled region where experimental data are scarcely known. Secondly, the solid–liquid surface tension $\sigma_0^{SL}(T)$ cannot be measured directly and it is usually determined from the analysis of the experimental data for the nucleation rate in supercooled liquid [2]. Therefore, the numerical value of the surface tension obtained by this way depends strongly on the theoretical model used in the analysis [9].

For the representation of the thermodynamic properties of supercooled water, the IAPWS-95 formulation [19] is recommended as being the most accurate. The melting temperature T_m was calculated with the international equation developed by Wagner et al. [24], while for the calculation of the ice density, $\rho_S = 1/v_S$, and heat of fusion, Δh, we used the vapor pressure formulation for ice developed by Wexler [25]. The surface tension $\sigma_0^{SL}(T)$ was calculated with Turnbull's expression [26]

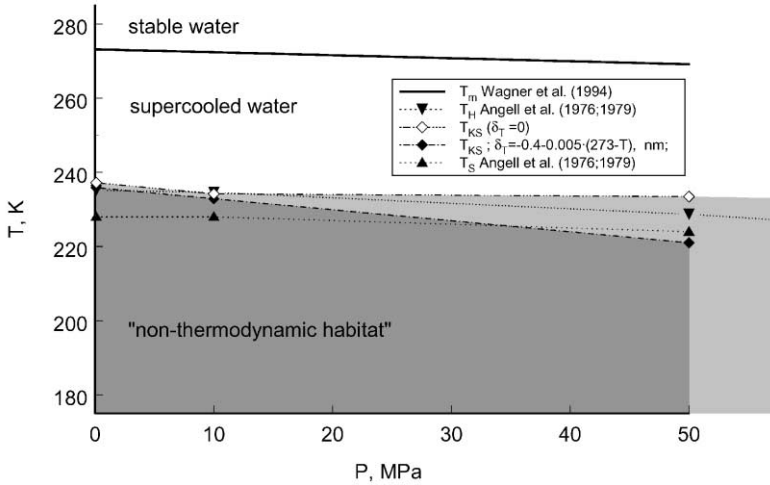$$\sigma_0^{SL} = \alpha \frac{\Delta h}{v_S^{2/3}} \tag{17}$$

Fig. 3. The phase diagram of supercooled water. The solid line represents the melting curve [24], the diamonds and filled triangles down with eye-guide lines correspond to the kinetic spinodal temperatures, T_{KS}, calculated with Eq. (7) with different approximations for the Tolman length δ_T, and the symbols represent the homogeneous nucleation, T_H (empty triangles down), and spinodal, T_S (triangles up), temperatures obtained by Angell et al. [22,23].

with $\alpha = 0.32$ as originally recommended for water by Turnbull [26]. A recent study [16] indicates that the Tolman length for the ice–water interface is negative and strongly depends on temperature. Therefore, here we calculated the kinetic spinodal with the temperature dependent Tolman length $\delta_T(T) = -0.4 - 0.005(273 - T)$, which is a simple linear interpolation of the results presented in Ref. [16] (see Fig. 2 in Ref. [16]).

The results of our calculations are compared with experimental data for the homogeneous nucleation temperatures T_H of Angell and co-workers [22,23] in Fig. 3. The open diamonds with the eye-guide lines in Fig. 3 correspond to the kinetic spinodal calculated with $\delta_T = 0$, while the filled diamonds correspond to the kinetic spinodal calculated with the temperature dependent Tolman length $\delta_T = \delta_T(T)$. The filled triangles up in Fig. 3 represent the values of the spinodal temperatures T_S obtained by Angell et al. [22,23] from the analysis of their isothermal compressibility data with the empirical expression

$$K_T = A_\kappa (T/T_S - 1)^{-\gamma_\kappa} \tag{18}$$

were A_κ, γ_κ, and T_S are the adjustable parameters. As one can see from Fig. 3, at pressures $P \leqslant 10$ MPa the curvature effect in supercooled water is not significant. At these pressures, both the kinetic spinodals, calculated with $\delta_T = 0$ and $\delta_T = \delta_T(T)$, lie very close to each other, and practically coincide with the homogeneous nucleation limit. However, at higher pressures, $P > 10$ MPa, T_{KS} calculated with $\delta_T = 0$ lies above the nucleation limit obtained by Angell and co-workers [22,23], while for $\delta_T = \delta_T(T)$ the kinetic spinodal lies systematically lower than T_H. At $P = 50$ MPa, T_{KS} calculated with $\delta_T = \delta_T(T)$ lies even lower than T_S reported by Angell et al. [22,23]. Since T_{KS} always

satisfies the obvious condition $T_S < T_{KS} \leqslant T_H$, or equivalently $(u_2)_S < (u_2)_{KS} < (u_2)_H$, it indicates that the IAPWS-95 formulation [19] for water and the empirical expression (18) are thermodynamically inconsistent in this region. As we mentioned above, the IAPWS-95 formulation [19] yields an accurate representation of the experimental data for pure water in a wide range of the parameters of state, including the supercooled water. Unfortunately, this empirical equation of state (EOS) gives some unphysical behavior if one tries to extrapolate it into the supercooled region beyond the range of the experimental data used for its optimization. Because of that, we were unable to calculate with the IAPWS-95 formulation [19] the kinetic spinodal for $\delta_T = \delta_T(T)$ at higher pressures, $P > 50$ MPa. For this goal, a more physical EOS for supercooled water should be used.

The kinetic spinodal represents the boundary behind which no equilibrium thermodynamic state can exist; therefore, we consider here the lowest temperatures (i.e., T_{KS} calculated with temperature dependent Tolman length) as a physical boundary of metastable states in supercooled water. The shaded area in Fig. 3 marks the region where no thermodynamic state for liquid water is possible. This is a "non-thermodynamic habitat" for liquid water because in this region the lifetime of the homogeneous state is smaller than the time to establish local equilibrium. Therefore, any equilibrium homogeneous state for liquid water is not possible in this region. The parameter u_2 in Eq. (2), or equivalently the first derivative $\bar{\mu}_\rho$, remains small but positive in this region. As consequence, the kinetic spinodal always appears earlier than the thermodynamic stability limit determined by the condition $\bar{\mu}_\rho = 0$.

The kinetic boundary of metastable states is mostly determined by the EOS applied for its prediction. Therefore, it is interesting to see what predictions can be made with other, less accurate, but more physical models. As example, we have used the new analytical (NA) equation of state for supercooled water developed recently by Jeffery and Austin [27]. This equation predicts the existence of a second critical point (CP$_2$) related to low density water (LDW)–high density water (HDW) phase equilibrium, and qualitatively reproduces the anomalous behavior of the isothermal compressibility in supercooled water. However, the quantitative difference between experimental data of Angell and co-workers [22,23], and calculated values of the isothermal compressibility in supercooled water is significant (see discussion in Ref. [11]). Therefore, one cannot expect to obtain with this EOS a good quantitative prediction of the physical boundary of metastable state in supercooled water. In this case, it is only the qualitative analysis is that of interest.

The phase diagram and the kinetic spinodal calculated with the NA EOS are shown in Fig. 4. The principle difference between this diagram and the phase diagram shown in Fig. 3 is that since Eq. (7) now has two roots, T_{KS1} and T_{KS2}, the "non-thermodynamic habitat" for supercooled liquid water now has a shape of a belt. It is interesting to note, that, according to this scenario, there are no thermodynamically unstable states in the supercooled water at pressures $P < 90$ MPa and temperatures from the melting curve down to $T = 150$ K. In this case, the pressure-dependent Kauzman temperature T_K gives a thermodynamic limit of stability in supercooled liquids [3]. However, the
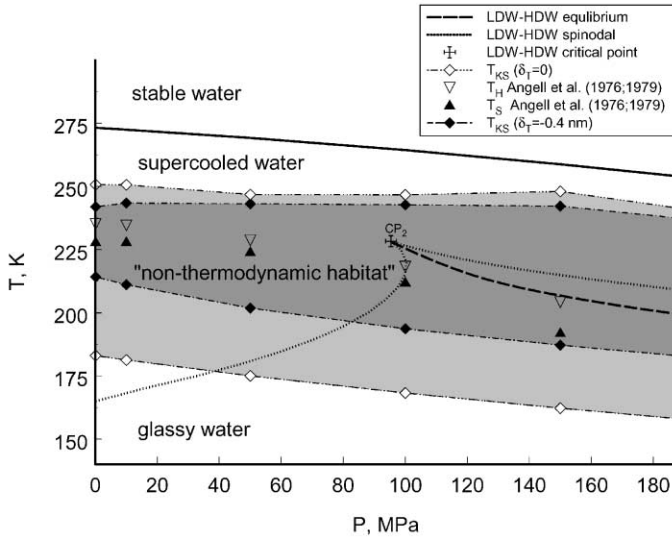
Fig. 4. The phase diagram of supercooled water calculated with the new analytic equation of state of Jeffery and Austin [27]. The cross corresponds to the critical point of LDW–HDW equilibrium (dashed curve), the dotted curves correspond to the LDW–HDW spinodals. The other legend as in Fig. 3.

Kauzman temperature T_K is not attainable experimentally because of the glass transition, which appears at temperatures $T_K < T_g < T_H$ [3]. According to the specification introduced by Mishima and Stanley [28], the temperature range $T_g < T < T_H$ belongs to the so called "no man's land", which corresponds to the short lived and, therefore, experimentally not attainable but still thermodynamic-metastable states. In our theory, no thermodynamic states exist inside the "non-thermodynamic habitat" belt (the temperature range $T_{KS2} < T < T_{KS1}$) which splits the "no man's land" into the two narrow strips, $T_g < T < T_{KS2}$ and $T_{KS1} < T < T_H$.

The glass transition temperature is essentially the temperature at which the relaxation time of the system is of the same order of magnitude as the observation time [29,30]. The ratio t_M/t_R calculated with NA EOS as a function of the temperature at $P = 0.1$ MPa is shown in Fig. 5. As one can see, at the temperatures $T_{KS1} < T < T_{KS2}$, which correspond to the "non-thermodynamic habitat", this ratio is much less than unity. At $T \cong T_{KS2}$ the ratio t_M/t_R is of order of one; therefore, the second kinetic spinodal temperature T_{KS2} can be interpreted as the high-temperature limit, T_g^{max}, for glassy, or ultraviscous, states. At higher temperatures $T > T_g^{max}(P)$ up to $T = T_{KS1}$ no glassy, ultraviscous, or any other thermodynamic metastable state is possible. The second critical point and the LDW–HDW coexistence curve lie inside the "non-thermodynamic habitat" belt, and, therefore, have no real physical meaning and in principle cannot be observed experimentally. Only the transparent area in Figs. 4 and 5 is available for experimental study.
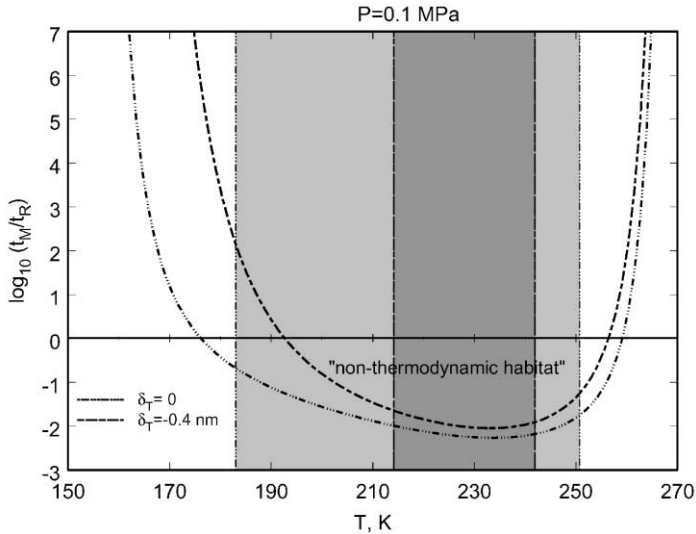
Fig. 5. The ratio t_M/t_R at $P = 0.1$ MPa for supercooled water as a function of temperature T calculated with the new analytic equation of state of Jeffery and Austin [27] with different values of the Tolman length δ_T.

5. Discussion

In the present work, we have developed a general, theoretical model for predicting of the physical boundary of metastable states—kinetic spinodal in superheated, stretched, and supercooled fluids. A unique feature of this model is that it takes into account of the curvature of the surface tension. This model does not contain adjustable parameters and requires only the equation of state and surface tension for the prediction of the kinetic spinodal in metastable liquids.

Here we have applied this method for the calculation of the kinetic spinodal in metastable water. We show that in the critical region, the curvature effect on the kinetic spinodal in superheated water is small. However, in stretched water, this effect is essential and it causes increasing of the surface tension and nucleation. In superheated and stretched water, the kinetic spinodal lies above the thermodynamic spinodal and qualitatively reproduces its shape. Starting from the critical point, the kinetic spinodal first traces the physical boundary of the metastable states in superheated water, then passes through negative pressures defining the limit of stability in stretched water. The theory is in good agreement with experimental data.

Although water is the most common and best-studied liquid, the peculiar behavior of its physical properties in supercooled regime is still a puzzle for investigators [21]. Only during the last 4 or 5 years a number of different models and equations of state for supercooled water have been developed [27,31–37]. In this work, using the IAPWS-95 formulation [19] for the representation of the thermodynamic properties of supercooled

water, we show that the curvature effect in supercooled water at high pressures and low temperatures is significant. Taking into account this effect, we obtained reasonably good agreement of the predicted kinetic spinodal with experimental limit of stability data obtained by Angell and co-workers [22,23]. However, the empirical IAPWS-95 formulation [19] cannot be extrapolated very far into the metastable region and it does not predict an existence of a glassy transition in supercooled water.

The less accurate but more physically attractive NA EOS developed by Jeffery and Austin [27] predicts existence of a second critical point and yields two kinetic spinodals in supercooled water. The question about the existence of a second critical point in supercooled water has been intensively discussed during the last 5–7 years and the discussion remains open (see Refs. [31–35,38,39]). Here, using the NA EOS as an example, we show that this question cannot be in principle resolved experimentally, and, therefore, it is physically irrelevant. Since the second critical point, CP_2, is always lying in the "non-thermodynamic habitat", it is not a real critical point, which can be observed, but rather a "virtual critical point", which rigorously speaking has no physical meaning. Nevertheless, the concept of a second—"virtual critical point" can be very useful, if it yields a good representation of the thermodynamic properties of supercooled water outside the "non-thermodynamic habitat". The second kinetic spinodal, T_{KS2}, generated with this "virtual critical point" can be associated with the upper temperature limit for the ultroviscous or glassy states. We presented here only qualitative prediction of this limit. As one can see from Fig. 5, the kinetic spinodal determined from Eq. (7) differs from the exact condition $t_M = t_R$, or, alternatively,

$$\frac{\lambda_0}{4\pi\gamma} = \exp\left[\frac{\gamma W_{\min}(T_{KS})}{k_B T}\right] \ . \tag{19}$$

Using Eqs. (3), (5), and (6), this condition can be written in the form

$$\frac{\lambda_0}{4\pi} \frac{\bar{\mu}_{\rho\rho}^2(T_{KS})}{\bar{\mu}_{\rho}^{3/2}(T_{KS})} \left(\frac{\rho}{\rho^*}\right)^{1/2} = \exp\left[\frac{4W_{\min}(T_{KS})\bar{\mu}_{\rho}^{3/2}(T_{KS})}{k_B T \bar{\mu}_{\rho\rho}^2(T_{KS})}\left(\frac{\rho^*}{\rho}\right)^{1/2}\right] \ . \tag{20}$$

Therefore, the physical boundary of metastable states in liquids should be determined from a solution of Eq. (20) rather than from Eq. (7). However, we need to note that since the Patashislii–Shumilo theory is valid only when $2\pi W_{\min}\gamma \gg k_B T$ [5], the physical boundary of metastable states, the kinetic spinodal T_{KS}, in this theory can be determined only approximately. Therefore, in practice, both the estimates with Eqs. (20) and (7) should be analyzed.

A comparison of the kinetic spinodals for the NA EOS calculated with Eqs. (20) and (7) is shown in Fig. 6. As one can see, the kinetic spinodal temperatures T_{KS1} and T_{KS2} calculated with Eq. (20) (open squares) give a wider "non-thermodynamic habitat" belt than one obtained with Eq. (7) (filled diamonds). As it was pointed out earlier by Kiselev [11], in spite of that the NA EOS gives interesting qualitative predictions, the quantitative predictions made with this EOS are incorrect. The NA EOS gives the second critical point $T_{c2} = 228.3$ K and $P_{c2} = 95.3$ MPa which is about 10 K
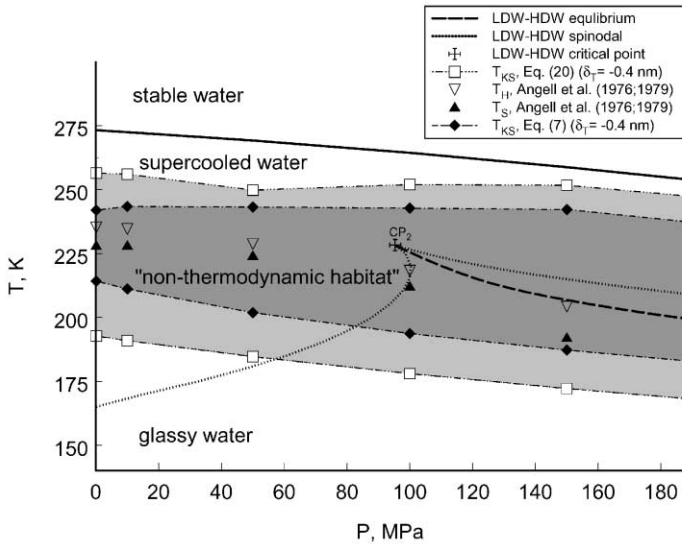
Fig. 6. The phase diagram of supercooled water calculated with the new analytic equation of state of Jeffery and Austin [27] and $\delta_T = -0.4$ nm. The empty squares correspond to the kinetic spinodals calculated with Eq. (20), and the diamonds correspond to the values calculated with Eq. (7). The other legend as in Fig. 3.

higher than the experimental homogeneous nucleation temperature obtained at this pressure by Kanno and Angel [23]. Therefore, the temperatures T_{KS1} calculated with the NA EOS lie systematically above T_H obtained by Angell and co-workers [22,23]. For example, at $P = 0.1$ MPa the temperature T_{KS1} calculated with the NA EOS and Eq. (20) is about 21 K higher than the homogeneous nucleation temperature T_H obtained by Speedy and Angell [22]. After a shift of the second kinetic spinodal temperature $T_{KS2} = 192$ K at the same value, one obtains $T_{KS2}^{shift} = 171$ K, which is a reasonable estimate for the upper limit for ultraviscous water at this pressure [28]. In order to provide a more accurate comparison with experimental data and give better predictions of the upper glass-transition temperature T_g^{max} for supercooled water, we need both a better EOS and more reliable estimate of the Tolman length.

The ultraviscous, or glassy, states are usually associated with the anomalous increasing of the relaxation time [3,30]. Therefore, for an independent estimate of the upper glass transition temperature T_g^{max} it would be extremely interesting to study how the transport coefficient Γ_c and, as consequence, the relaxation time t_R in Eq. (3) depends on the temperature in supercooled liquids. We expect that the decoupled-mode theory successfully applied earlier to the describing of the transport phenomena of pure fluids and binary mixtures in the extended critical region [40,41] can be also applied in supercooled liquids. Research towards the application of this approach to glassy states is in progress, and the results will be presented in future publications.

Acknowledgements

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