Physical limit of stability in supercooled D_2O and D_2O+H_2O mixtures

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The fluctuation theory of homogeneous nucleation was applied for calculating the physical boundary of metastable states, the kinetic spinodal, in supercooled D_2O and D_2O+H_2O mixtures. The kinetic spinodal in our approach is completely determined by the surface tension and equation of state of the supercooled liquid. We developed a crossover equation of state for supercooled D_2O, which predicts a second critical point of low density water–high density water equilibrium, CP_2, and represents all available experimental data in supercooled D_2O within experimental accuracy. Using Turnbull's expression for the surface tension we calculated with the crossover equation of state for supercooled D_2O the kinetic spinodal, T_{KS}, which lies below the homogeneous nucleation temperature, T_H. We show that CP_2 always lies inside in the so-called ''nonthermodynamic habitat'' and physically does not exist. However, the concept of a second ''virtual'' critical point is physical and very useful. Using this concept we have extended this approach to supercooled D_2O+H_2O mixtures. As an example, we consider here an equimolar D_2O+H_2O mixture in normal and supercooled states at atmospheric pressure, $P=0.1$ MPa. © *2003 American Institute of Physics.*
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I. INTRODUCTION

In the fluctuation theory of homogeneous nucleation,[1,2] the physical boundary of metastable states is determined from the condition that the lifetime of the metastable phase t_M is of the same order as a relaxation time of a homogeneous state t_R. Therefore, in the vicinity of the thermodynamic spinodal $t_M \ll t_R$, the very concept of a ''homogeneous'' state loses its meaning and the thermodynamic spinodal is experimentally unattainable. The line where $t_M \cong t_R$ is treated in the fluctuation theory of homogeneous nucleation as the kinetic spinodal. Both times, t_M and t_R, depend on the kinetic properties of liquid, but the ratio t_M/t_R depends on the thermodynamic properties only.

In our previous work,[3–7] we developed a general, based on the fluctuation theory of homogeneous nucleation[1,2] approach for the calculation of the physical boundary of metastable states in superheated, stretched, and supercooled liquids. The kinetic spinodal in our approach is completely determined by the surface tension and equation of state (EOS) of the metastable fluid. In our most recent work,[7] further referred as Paper I, we applied this approach for the calculation of the kinetic spinodal in supercooled water. Using the two-critical point (TCP) scenario,[8–18] we developed a parametric crossover model for supercooled water and have shown that the second critical point of the low density water (LDW)–high density water (HDW) equilibrium, CP_2, always lies inside the so-called ''nonthermodynamic habitat'' created by this ''virtual'' critical point itself, and, therefore, does not exist. Nevertheless, the concept of the second ''virtual'' critical point is useful and yields a physically self-consistent representation of the kinetic spinodal and thermodynamic properties of supercooled water outside the ''nonthermodynamic habitat'' region.

In this work, we continue the study initiated in our previous papers for supercooled water[5–7] and extend this approach to supercooled D_2O and D_2O+H_2O mixtures. We proceed as follows: In Sec. II we review the major concepts of the fluctuation theory of homogeneous nucleation. In Sec. III we describe a phenomenological crossover model for one-component fluids and obtain a crossover EOS for pure D_2O. An application of this crossover EOS to the prediction of the kinetic spinodal in pure D_2O is presented in Sec. IV. In Sec. V we describe the isomorphic crossover free-energy model for binary mixtures and consider its application to the prediction of the kinetic spinodal in supercooled D_2O+H_2O mixtures. Our results are discussed and summarized in Sec. VI.

II. THEORETICAL BACKGROUND

According to classical theory of homogeneous nucleation[19–21] the nucleation rate J, which determines the average number of nuclei formed in a unit volume of the metastable phase per unit time, is proportional to the probability of having a critical nucleus

$$J = J_0 \exp(-W_{\min}/k_B T), \tag{2.1}$$

where k_B is Boltzmann constant, and

$$W_{\min} = \tfrac{4}{3}\pi r_c^2 \sigma \tag{2.2}$$

determines the nucleation barrier, which is equal to the minimum reversible work required to form a critical size nucleus. σ is the surface tension, and J_0 is a prefactor which depends on a kinetic coefficient, usually the self-diffusion or the shear viscosity, but does not depend on the critical radius r_c. The mean time of formation of a critical nucleus in a volume V,

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$$t_M=(JV)^{-1}=(J_0V)^{-1}\exp(W_{\min}/k_BT), \tag{2.3}$$

determines the lifetime of the metastable state. The homogeneous nucleation limit of the metastable state is determined as a locus of the constant (usually small $t_M\simeq 0.1\div 1$ seconds[20]) lifetime t_M. Thus, in the classical theory of homogeneous nucleation, the nucleation temperature T_H is determined by both, the thermodynamic (through the $W_{\min}$) and kinetic (through the J_0), properties of supercooled fluid.

In the fluctuation theory of homogeneous nucleation,[1,2] the dynamics of a system in a metastable state of the initial phase are connected with the relaxation and fluctuation of the hydrodynamic fields of the order parameter $\varphi(\vec{x},t)$, energy density $\epsilon(\vec{x},t)$, etc. The slowness of their relaxation allows us to exclude other degrees of freedom and to only consider the dynamics of a single hydrodynamic mode-scalar field of the order parameter. In this case the equation of motion of the system is the same as that of a system near a second-order phase transition[22]

$$\frac{\partial\varphi}{\partial t}=-\Gamma_c\Delta\left(-\frac{\partial\mathcal{H}}{\partial\varphi}+f_{st}\right), \tag{2.4}$$

where Γ_c is a transport coefficient, $\mathcal{H}$ is an effective Hamiltonian, and f_{st} is an external random force modeling the thermal fluctuations. The effective Hamiltonian $\mathcal{H}\{\varphi\}$ can be expanded in a functional series as in a second-order phase transition. In the vicinity of instability region, the effective Hamiltonian can be represented in the form[2]

$$\mathcal{H}\{\varphi\}=\int\left(\frac{g}{2}(\Delta\varphi)^2+\frac{u_2}{2}\varphi^2-\frac{u_3}{3}\varphi^3\right)dV, \tag{2.5}$$

where g, u_2, $u_3>0$, and u_2 are 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. (2.4) and (2.5) obtained by Patashinskii and Shumilo[1,2] show that the lifetime of the metastable phase taking into account of fluctuations is given by

$$t_M=t_R\left(\frac{4\pi\gamma}{\lambda_0}\right)\exp(\gamma W_{\min}/k_BT), \tag{2.6}$$

where $t_R=16g/\Gamma_c u_2^2$ is a characteristic time governing the relaxation toward local equilibrium, $\gamma=(u_2g)^{3/2}/k_BTu_3^2$ is a dimensionless parameter and $\lambda_0\cong 8.25$ is a dimensionless constant. It follows from Eq. (2.6) that when $\gamma W_{\min}\gg k_BT$ the lifetime of the metastable phase is exponentially longer than the relaxation time t_R. For $\gamma\leqslant k_BT/W_{\min}$, the initial homogeneous state that is stable with respect to long-wavelength fluctuations transforms to a heterogeneous state as a result of fluctuations during a time comparable with the time governing the relaxation toward local equilibrium ($t_M\simeq t_R$). The curve $\gamma W_{\min}=k_BT$, or, alternatively,

$$(u_2)_{KS}=u_2(T_{KS})=\frac{1}{g}\left(\frac{k_BT_{KS}u_3^2}{W_{\min}}\right)^{2/3}, \tag{2.7}$$

can be regarded as the physical limit of stability in a supercooled liquid—the kinetic spinodal, T_{KS}, limits the region in the phase diagram [$u_2>(u_2)_{KS}$ or $T>T_{KS}$] of statistically well defined and experimentally attainable metastable states. For $0<u_2<(u_2)_{KS}$ (or $T<T_{KS}$) 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 one-component fluids.[1,2]

As was shown by Kiselev,[4,5] the parameters u_2 and u_3 in the effective Hamiltonian (2.5) for one-component fluids can be expressed through the dimensionless first, $\bar{\mu}_\rho=\rho(\partial\mu/\partial\rho)_T/k_BT$, and second, $\bar{\mu}_{\rho\rho}=\rho^2(\partial^2\mu/\partial\rho^2)_T/k_BT$, derivatives of the chemical potential, $\mu=(\partial\rho A/\partial\rho)_T=A+P/\rho$, with respect to the density, ρ,

$$\begin{aligned}u_2&=k_BT\rho\bar{\mu}_\rho=\rho\left(\frac{\partial P}{\partial\rho}\right)_T,\\ u_3&=\frac{1}{2}k_BT\rho\bar{\mu}_{\rho\rho}=\frac{1}{2}\rho\left[-\left(\frac{\partial P}{\partial\rho}\right)_T+\rho\left(\frac{\partial^2P}{\partial\rho^2}\right)_T\right],\end{aligned} \tag{2.8}$$

and for the parameter g in supercooled liquids a good estimate is[5–7]

$$g=k_BT\rho_{tr}^{1/3}, \tag{2.9}$$

where ρ_{tr} is the density of liquid at the triple point. Using Eqs. (2.8) and (2.9), Eq. (2.7) for the kinetic spinodal T_{KS} can be written in the form[5,6]

$$\bar{\mu}_\rho(T_{KS})=\left[\frac{k_BT\bar{\mu}_{\rho\rho}^2(T_{KS})}{4W_{\min}(T_{KS})}\right]^{2/3}\left(\frac{\rho}{\rho_{tr}}\right)^{1/3}. \tag{2.10}$$

We need to note that Eq. (2.10) for the kinetic spinodal T_{KS}, unlike Eq. (2.3) for the homogeneous nucleation limit T_H, does not contain any kinetic coefficient. Along the kinetic spinodal the lifetime of the metastable phase t_M and the relaxation time t_R are changed, but the ratio t_M/t_R, which depends on the thermodynamic properties of liquid only, remains constant. Therefore, if the surface tension is known, the physical boundary of metastable states, the kinetic spinodal, in the fluctuation theory of homogeneous nucleation is completely determined by the equation of state, $P=P(\rho,T)$.

III. EOS FOR SUPERCOOLED D_2O

In Paper I we have shown that the second HDW–LDW critical point, CP_2, is actually a ''virtual'' critical point which physically does not exist. However, the concept of a second critical point appears to be very useful and the parametric crossover model in combination with the two-critical point scenario yields a highly accurate and physically self-consistent representation of all available experimental data and the kinetic spinodal in supercooled water. Therefore, for supercooled D_2O we also adopt the TCP scenario and parametric crossover model employed earlier for supercooled H_2O.[7]

The Helmholtz free energy in the parametric crossover model is represented in the form

$$\bar{A}(T,\rho)=\Delta\bar{A}(\tau,\Delta\eta)+(\rho/\rho_c)\bar{\mu}_0(T)+\bar{A}_0(T), \tag{3.1}$$

where $\Delta\bar{A}$ is the critical part of the dimensionless Helmholtz free energy density $\bar{A}=\rho A/\rho_cRT_c$ (where R is the universal

gas constant) as a function of $\tau = T/T_c - 1$, the dimensionless deviation of the temperature T from the critical temperature T_c, and the order parameter $\Delta\eta = \Delta\rho = \rho/\rho_c - 1$, the dimensionless deviation of the density ρ from the critical density ρ_c, while the background contributions $\overline{\mu}_0(T)$ and $\overline{A}_0(T)$ are analytic functions of temperature. The critical part of the Helmholtz free energy is given by[23–26]

$$\Delta\overline{A}(r,\theta) = kr^{2-\alpha}R^{\alpha}(q) \times\left[a\Psi_0(\theta^2) + \sum_{i=1}^{5} c_i r^{\Delta_i} R^{-\overline{\Delta}}(q)\Psi_i(\theta)\right], \qquad (3.2)$$

$$\tau = r(1-b^2\theta^2), \quad \Delta\rho = kr^{\beta}R^{-\beta+1/2}(q)\theta + d_1\tau, \qquad (3.3)$$

where β, α, and Δ_i are the universal critical exponents,[27,28] b^2 is a universal linear-model parameter, the scaled functions $\Psi_i(\theta)$ are universal analytic (even for $i=0-2$, or odd for $i=3-5$) functions of the parametric variable θ, and k, d_1, a, and c_i are system-dependent coefficients. The crossover function $R(q)$ in Eqs. (3.2) and (3.3) is defined by the expression

$$R(q) = \left(1 + \frac{q^2}{1+q}\right)^2, \qquad (3.4)$$

where the crossover variable q is related to the parametric variable r by

$$q = (rg)^{1/2}, \qquad (3.5)$$

where $g = \mathrm{Gi}^{-1}$ is the inverse Ginzburg number.

The first three terms on the right-hand side of Eq. (3.2) correspond to the asymptotic ($i=0$), first ($i=1$), and second ($i=2$) Wegner correction terms.[29] The next two asymmetric terms ($i=3$ and $i=4$) are equivalent to a "mixing" of the thermodynamic variables related to the asymmetry of the VLE surface in real fluids with respect to the critical isochore,[30,31] and the last term in Eq. (3.2) ($i=5$) corresponds to the additional asymmetric term $\propto\Delta\eta^5$ in the effective Hamiltonian of the system.[32,33] For large values of the variable q, at $|\tau| \gg \mathrm{Gi}$, the crossover function $R(q)$ modifies each term in Eq. (3.2) so they all become analytic, and Eq. (3.2) is transformed into the classical Landau expansion[34] with additional asymmetric terms[25] $\propto\Delta\eta^3$ and $\Delta\eta^5$.

In order to apply the parametric crossover model to real systems, one needs to specify the background contributions in Eq. (3.1). Here, following our previous work for supercooled water,[7] we represent the analytic functions $\overline{\mu}_0(T)$ and $\overline{A}_0(T)$ by truncated Taylor expansions

$$\overline{\mu}_0(T) = \sum_{j=1}^{3} m_j\tau^j, \qquad \overline{A}_0(T) = -Z_c + \sum_{j=1}^{3} A_j\tau^j, \qquad (3.6)$$

where $Z_c = P_c/\rho_c RT_c$ is the critical compressibility. The parametric crossover (CR) EOS in this case is completely specified by Eqs. (3.2)–(3.6) and contains the following universal constants: the critical exponents α, β, Δ_i, and $\tilde{\Delta}_i$, and the linear-model parameter b^2. The values of all universal constants and the universal scaled functions $\Psi_i(\theta)$ are presented in Tables I and II, respectively. In addition, the parametric CR EOS also contains the following system-dependent constants: critical parameters T_c, ρ_c, and P_c, the rescaled asymptotic critical amplitude k of the coexistence curve, the amplitude a of the asymptotic term, the amplitudes c_i of the nonasymptotic ($i=1,2$) and asymmetric ($i=3-5$) terms, the inverse rescaled Ginzburg number g, and the coefficients m_j and A_j in the background contributions. The coefficient c_5 corresponds to the asymmetric term $\propto\Delta\eta^5$, which appears to be statistically irrelevant,[23,24,26] therefore we further set $c_5 \equiv 0$.

TABLE I. Universal scaled functions.

$\Psi_0(\theta) = \frac{1}{2}b^4[2\beta(b^2-1)/(2-\alpha) + 2\beta(2\gamma-1)(1-b^2\theta^2)/(\gamma(1-\alpha)) - (1-2\beta)(1-b^2\theta^2)^2/\alpha]$
$\Psi_1(\theta) = [1/(2b^2(1-\alpha+\Delta_1))][(\gamma+\Delta_1)/(2-\alpha+\Delta_1) - (1-2\beta)b^2\theta^2]$
$\Psi_2(\theta) = [1/(2b^2(1-\alpha+\Delta_2))][(\gamma+\Delta_2)/(2-\alpha+\Delta_2) - (1-2\beta)b^2\theta^2]$
$\Psi_3(\theta) = \frac{1}{3}\theta[3 - 2(e_0-\beta)b^2\theta^2 + e_1(1-2\beta)b^4\theta^4]$
$\Psi_4(\theta) = \frac{1}{3}b^2\theta^3[1 - e_2(1-2\beta)b^2\theta^2]$
$\Psi_5(\theta) = \frac{1}{3}b^2\theta^3[1 - e_4(1-2\beta)b^2\theta^2]$

As was pointed out in our previous study for supercooled water,[7] an accurate determination of the position of the CP2, especially the critical pressure P_{c2} for which an uncertainty is of about 10%–15%, is not possible in principle. Therefore, in order to avoid an over fitting, for supercooled D_2O we adopt the same value of P_{c2} as obtained earlier for supercooled H_2O.[7] All other system-dependent constants for supercooled D_2O, including the critical parameters T_{c2} and ρ_{c2}, have been found from a fit of the CR EOS to experimental data. For this purpose the experimental κ_T data by Kanno and Angell,[35] experimental C_P data by Angell *et al.*[36] and by Rasmunssen and MacKenzie,[37] and experimental (ρ,T) data by Zheleznyi,[38] by Kanno and Angell,[39] and by Hare and Sorensen[40] have been used. In addition, we also used the specific volume data in the stable region at temperatures $T_m \leqslant T \leqslant 300$ and pressures $1 \leqslant P \leqslant 150$ MPa generated with the new International Formulation for the thermodynamic properties of heavy water of Kestin and

TABLE II. Universal constants.

α	0.110
β	0.325
$\gamma = 2-\alpha-2\beta$	1.24
$b^2 = (\gamma-2\beta)/\gamma(1-2\beta) \cong$	1.359
$\Delta_1 = \tilde{\Delta}_1$	0.51
$\Delta_2 = \tilde{\Delta}_2 = 2\Delta_1$	1.02
$\Delta_3 = \Delta_4 = \gamma+\beta-1$	0.565
Δ_5	1.19
$\tilde{\Delta}_3 = \tilde{\Delta}_4 = \Delta_3 - 1/2$	0.065
$\tilde{\Delta}_5 = \Delta_5 - 1/2$	0.69
$e_0 = 2\gamma+3\beta-1$	2.455
$e_1 = (e_0-\beta)(2e_0-3)/(e_0-5\beta) \cong$	4.90
$e_2 = (e_0-3\beta)/(e_0-5\beta) \cong$	1.773
$e_3 = 2-\alpha+\Delta_5$	3.08
$e_4 = (e_3-3\beta)/(e_3-5\beta) \cong$	1.446
$\Delta_s = \gamma+\beta-1-\Delta_1 \cong$	0.055

Sengers.[41] We found that the best estimates for the critical parameters of the second critical point CP_2 in supercooled D_2O are

$$T_{c2}=195\pm 5 \text{ K},$$
$$\rho_{c2}=1220\pm 50 \text{ kg m}^{-3}, \tag{3.7}$$
$$P_{c2}=230\pm 20 \text{ MPa}.$$

It appears, that with respect to the CP_2 all available experimental data for supercooled D_2O lie in the high temperature–low density region ($T>T_{c2}$ and $\rho<\rho_{c2}$). Therefore, an extrapolation of the CR EOS with the asymmetric terms obtained from the ''high temperature–low density'' fit into the low temperature–high density region ($T\leqslant T_{c2}$ and $\rho\geqslant\rho_{c2}$) can give some unphysical behavior and, in general, is not recommended. In order to reduce the number of the adjustable parameters and make model more predictable at high densities, in the second step we, following Kiselev and Kostyukova,[3] represented the asymmetric amplitude c_4 in Eq. (3.2) as a linear combination of the amplitudes c_1 and c_3,

$$c_4=c_1\frac{C_0}{E_0}-c_3\frac{D_0}{E_0}, \tag{3.8}$$

where the coefficients C_0, D_0, and E_0 depend on the critical exponent only

$$C_0=\frac{(\gamma+\Delta_1)}{\sqrt{b^2(1-2\beta)}}\left(\frac{2\beta}{1-2\beta}\right)^{\Delta s}, \tag{3.9}$$

$$D_0=e_0-\beta+e_1\frac{(e_0-5\beta)}{(1-2\beta)^2}, \tag{3.10}$$

$$E_0=1-\frac{(1-e_0+2e_2+\beta)}{(1-2\beta)}+e_2\frac{(e_0-\beta-2)}{(1-2\beta)^2}. \tag{3.11}$$

Comparison of the constrained, by Eq. (3.8), crossover model CREOS-02 and unconstrained crossover model CREOS-01 with experimental data for supercooled D_2O is shown in Figs. 1–3. As one can see, in the entire experimentally attainable region both CREOS-01 and CREOS-02, models are practically equivalent. Both models represent the experimental values of the isothermal compressibility κ_T in liquid and supercooled D_2O in the pressure range $P=10-190$ MPa with an average absolute deviation (AAD) of about 1.5% ($n=72$), the specific heat and liquid densities data at $P=1$ MPa and temperatures 245 K$\leqslant T\leqslant$300 K with an AAD of about 1.0% ($n=38$) and 0.03% ($n=36$), respectively. However, since the constrained crossover model contains one adjustable parameter less than CREOS-01 and gives a physically more reliable extrapolation into the high-density region, we choose here the CREOS-02 as a basic EOS for supercooled D_2O. The values of all system-dependent parameters in the CREOS-02 for supercooled D_2O are listed in Table III. In the second column in Table III we also give the values of the system-dependent parameters in the CREOS-02 for supercooled H_2O. The values of these parameters have been obtained from a fit of the CREOS-02 to the experimental κ_T, $\rho(T)$, and C_P data for supercooled H_2O as was described in our previous work for CREOS-01.[7] Since in supercooled H_2O both models, CREOS-01 and CREOS-02, practically coincide, we will not discuss the CREOS-02 for H_2O here.

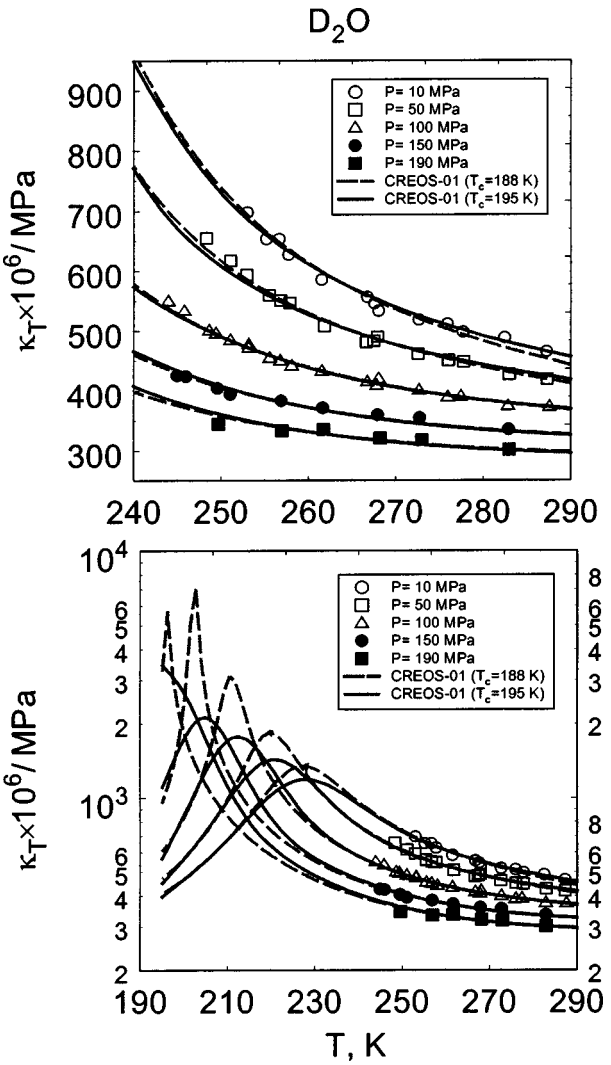

FIG. 1. The isothermal compressibility of D_2O at different pressures in normal and supercooled states as a function of temperature. The symbols represent experimental values obtained by Angell *et al.* (Ref. 35), the dashed curves represent values calculated with the CREOS-01, and the solid curves correspond to the values calculated with the CREOS-02.

IV. KINETIC SPINODAL IN SUPERCOOLED D_2O

Equation (2.10) for the kinetic spinodal requires the surface tension σ, which appears in Eq. (2.2) through the nucleation barrier $W_{\min}$. In general, the surface tension in one-component fluids can be considered as a function of the temperature and radius of curvature r. Here, following our previous work,[6,7] we represent the surface tension in the form

$$\sigma(T,r)=\sigma_0(T)\left(1-2\frac{\delta_T}{r}\right), \tag{4.1}$$

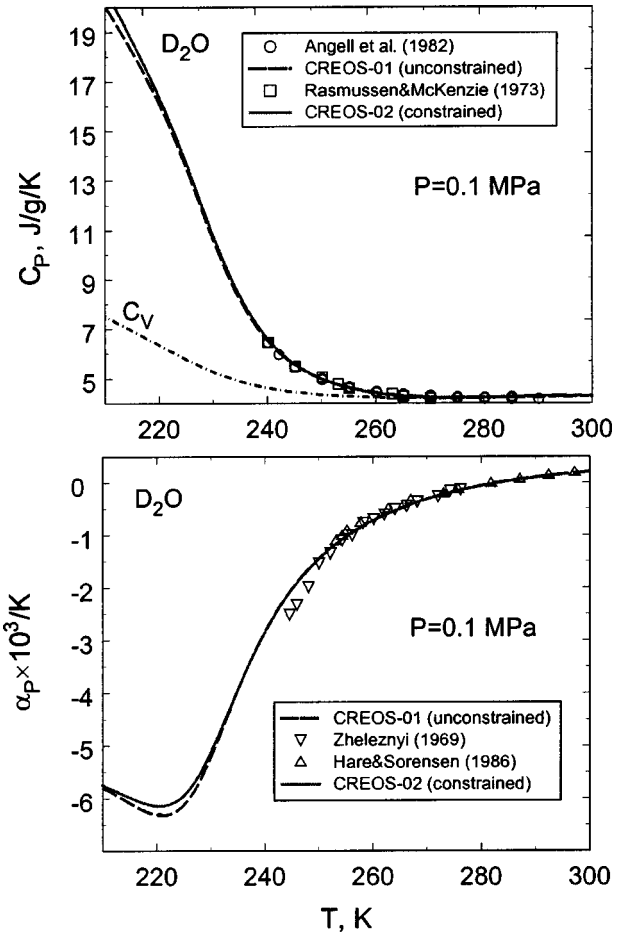

FIG. 2. The isobaric specific heat (top) and thermal expansivity (bottom) of D_2O at atmospheric pressure, $P=0.1$ MPa, in normal and supercooled states as a function of temperature. The symbols represent experimental values obtained by Angell *et al.* (Ref. 36) (circles), by Rasmussen and MacKenzie (Ref. 37) (squares), by Zheleznyi (Ref. 38) (triangles down), and by Hare and Sorensen (Ref. 40) (triangles up). The dashed curves represent values calculated with the CREOS-01, the solid curves correspond to the values calculated with the CREOS-02, and the dot–dashed curve represents values of the isochoric heat capacity calculated with the CREOS-02.

where δ_T is the Tolman length,[42] and σ_0 is a surface tension of the planar interface. The nucleation barrier, $W_{\min}$, and critical radius of the nucleus, r_c, in this case can be written in the form[6]

TABLE III. System-dependent parameters for the crossover EOS for supercooled D_2O and D_2O+H_2O mixtures.

Parameter	D_2O	H_2O	$k_i^{(1)}$
k	0.319 254	0.360 725	−3.482 67E+00
d_1	0.200 011	0.216 981	−6.756 78E−01
a	211.969	236.150	−2.313 05E+01
c_1	−379.046	−207.762	−3.344 92E+01
c_2	265.477	267.900	−1.151 41E+00
c_3	−407.576	−418.576	2.111 15E+01
c_4	−458.119	−2028.26	0
g	13.9632	15.7862	9.890 01E+00
A_1	−0.712 249	−0.204 735	9.096 81E+00
A_2	215.237	231.325	−3.337 98E+01
A_3	50.5706	53.9308	0
m_1	1.919 44	0.536 002	−2.692 77E+02
m_2	−155.576	−152.770	1.732 85E+01
m_3	−14.7238	−15.5989	−5.996 06E+00

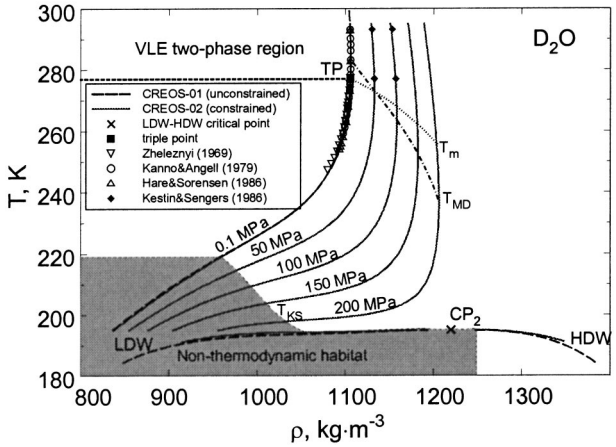

FIG. 3. $T-\rho$ diagram of supercooled D_2O. The symbols represent experimental values obtained by Zheleznyi (Ref. 38) (triangles down), by Kanno and Angell (Ref. 39) (circles), and by Hare and Sorensen (Ref. 40) (triangles up), and the diamonds correspond to the data generated with the new International formulation for the thermodynamic properties of heavy water of Kestin and Sengers (Ref. 41). The dashed curves represent values calculated with the CREOS-01, and the solid curves correspond to the values calculated with the CREOS-02.

$$W_{\min}=\frac{4}{3}\pi r_c^2\sigma_0\left(1-4\frac{\delta_T}{r_c}\right), \tag{4.2}$$

$$r_c=\frac{1}{2}r_c^0\left(1+\sqrt{1-4\frac{\delta_T}{r_c}}\right), \tag{4.3}$$

and the critical radius r_c^0 is given by

$$r_c^0=\frac{T_m\sigma_0(T)v_S(T)}{(T_m-T)\Delta h} \tag{4.4}$$

where v_S is the molar volume of solid at the melting temperature T_m, and Δh is the molar enthalpy of fusion. For surface tension at the planar solid–liquid interface, $\sigma_0(T)$, we have used Turnbull's expression[43]

$$\sigma_0=0.32\frac{\Delta h}{v_S^{2/3}}. \tag{4.5}$$

As follows from Eqs. (2.10), and (4.2)–(4.5), if the Tolman length, δ_T, is known, the kinetic spinodal in supercooled liquid is completely determined by the equation of state only. The results of our calculations for the kinetic spinodal in supercooled D_2O performed with CREOS-02 and $\delta_T=-0.2$ nm (which appears to be a reasonably good estimate for the supercooled water[6]) are shown in Figs. 3 and 4. The dotted curve in Figs. 3 and 4 corresponds to the melting temperatures, T_m, the dot–dashed curve represent the temperatures of the maximum densities, T_{MD}, calculated with the CREOS-02, and the dark-shaded area marks the ''nonthermodynamic habitat,'' i.e., the region where no thermodynamic state for supercooled D_2O is possible. As one can see, the second critical point, CP_2, lies inside the ''nonthermodynamic habitat'' for supercooled D_2O and, therefore, physically does not exist. However, outside the ''nonthermody-

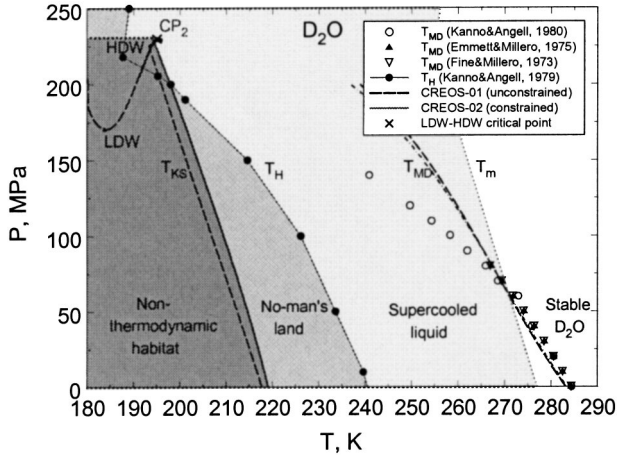

FIG. 4. $P-T$ diagram of supercooled D_2O. The symbols represent the homogeneous nucleation temperatures obtained by Kanno and Angell (Ref. 35) (filled circles with the eye-guide line), the temperatures of the maximum densities, T_{MD}, obtained by Kanno and Angell (Ref. 39) (circles), by Emmett and Millero (Ref. 59) (triangles up), and by Fine and Millero (Ref. 60) (triangles down). The dashed and solid curves correspond to the T_{MD} and the kinetic spinodals, T_{KS}, calculated with the CREOS-01 and with the CREOS-02, respectively.

namic habitat'' at $T>T_{KS}$, in the so-called ''no-man's land'' ($T_{KS}<T<T_H$), i.e., the region with short lived but still thermodynamic states[10] (the light-shaded area in Fig. 4), and in the experimentally attainable metastable region ($T>T_H$) CREOS-02 can be used for the accurate calculation of the thermodynamic properties of supercooled D_2O.

V. SUPERCOOLED D_2O+H_2O MIXTURES

A crossover expression for the Helmholtz free energy of binary mixtures can be obtained from the principle of critical-point universality,[44–47] which means that with the appropriately chosen thermodynamic variables, also called isomorphic variables, the thermodynamic potential of binary mixtures has the same form as the thermodynamic potential of a one-component fluid. An isomorphic crossover equation of state for binary mixtures based on the critical-point universality and phenomenological crossover model (3.2) has been developed by Kiselev.[26] This crossover model has been widely used for the prediction of the thermodynamic properties and the phase behavior of more than 25 binary mixtures,[26,48–51] including pure H_2O and D_2O and their binary mixtures,[52,53] in a wide range of the parameters of state around the critical point of the vapor–liquid equilibria, CP_1. Here, we apply this approach to the supercooled D_2O+H_2O mixtures.

The isomorphic free-energy density of a binary mixture is given by[26]

$$\rho\tilde{A}(T,\rho,\tilde{x})=\rho A(T,\rho,x)-\rho\overline{\mu}x(T,\rho,\tilde{x}), \tag{5.1}$$

where $\overline{\mu}=\mu_2-\mu_1$ is the difference of the chemical potentials μ_1 and μ_2 of the mixture components, $x=N_2/(N_1+N_2)$ is the mole fraction of the second component in the mixture, $\rho A(T,\rho,x)$ is the Helmholtz free-energy density of the mixture, and the isomorphic variable $\tilde{x}$ is given by

$$\tilde{x}=\frac{e^{\overline{\mu}/RT}}{1+e^{\overline{\mu}/RT}}. \tag{5.2}$$

The thermodynamic equation

$$x=-\tilde{x}(1-\tilde{x})\left(\frac{\partial\tilde{A}}{\partial\tilde{x}}\right)_{T,\rho}\frac{1}{RT} \tag{5.3}$$

provides a relation between the concentration x and the isomorphic variable $\tilde{x}$. At fixed $\tilde{x}$ the isomorphic free-energy $\rho\tilde{A}$ will be the same function of τ and ρ as the Helmholtz free-energy density of a one-component fluid. With Eqs. (3.2) and (3.3) the isomorphic free-energy density of binary mixtures reads[26]

$$\begin{aligned}\frac{\rho\tilde{A}(T,\rho,\tilde{x})}{R\rho_{c1}T_{c1}}=&\tilde{k}r^{2-\alpha}R^{\alpha}(q)\\&\times\left[\tilde{a}\Psi_0(\theta)+\sum_{i=1}^{4}\tilde{c}_i r^{\Delta_i}R^{-\tilde{\Delta}_i}(q)\Psi_i(\theta)\right]\\&+\sum_{i=1}^{4}\left(\tilde{A}_i+\frac{\rho}{\rho_c}\tilde{m}_i\right)\tau^i(\tilde{x})-\frac{P_c(\tilde{x})}{R\rho_{c1}T_{c1}}\\&+\frac{\rho T}{\rho_{c1}T_{c1}}[\ln(1-\tilde{x})+\tilde{m}_0],\end{aligned} \tag{5.4}$$

$$\tau=\frac{T-T_c(\tilde{x})}{T_c(\tilde{x})}=r(1-b^2\theta^2), \tag{5.5}$$

$$\Delta\rho=\frac{\rho-\rho_c(\tilde{x})}{\rho_c(\tilde{x})}=\tilde{k}r^{\beta}R^{-\beta+1/2}(q)\,\theta+\tilde{d}_1\tau, \tag{5.6}$$

where all nonuniversal parameters as well as the critical parameters $T_c(\tilde{x})$, $\rho_c(\tilde{x})$, and $P_c(\tilde{x})$ are analytic functions of the isomorphic variable $\tilde{x}$.

In addition to Eqs. (5.4)–(5.6), we also adopted a so-called critical line condition (CLC), which implies that a zero level of the entropy of a binary mixture can be chosen so that the isomorphic variable $\tilde{x}=x$ along the whole critical line, including the one-component limits.[54–58] For the thermodynamic potential as given by Eqs. (5.4)–(5.6), the CLC can be written in the form[26]

$$\frac{d\tilde{m}_0}{d\tilde{x}}=\frac{1}{R\rho_cT_c}\frac{dP_c}{d\tilde{x}}+\frac{\rho_{c1}}{\rho_c}(\tilde{A}_1+\tilde{m}_1)\frac{T_{c1}}{T_c^2}\frac{dT_c}{d\tilde{x}}, \tag{5.7}$$

$$T_c(\tilde{x})=T_c(x),\quad \rho_c(\tilde{x})=\rho_c(x),\quad P_c(\tilde{x})=P_c(x). \tag{5.8}$$

The critical values of the entropy $S=-(\partial\tilde{A}/\partial T)_{\rho,\overline{\mu}}$ and the enthalpy H in this case are determined by[51]

$$\frac{S_c}{R}=-\frac{\rho_{c1}T_{c1}}{\rho_cT_c}(\tilde{A}_1+\tilde{m}_1)-\tilde{m}_0$$

and

$$\frac{H_c}{RT_{c1}}=-\frac{\rho_{c1}}{\rho_c}(\tilde{A}_1+\tilde{m}_1). \tag{5.9}$$

Thus, the CLC in the form (5.7) does not put any restriction on the zero level of the enthalpy, and just determines the zero level of the entropy, which in binary mixtures can be chosen arbitrarily.

To specify the crossover equation for $\tilde{A}(T,\rho,\tilde{x})$ of a binary mixture, one also needs the system-dependent parameters $\tilde{d}_1(\tilde{x})$, $\tilde{k}(\tilde{x})$, $\tilde{a}(\tilde{x})$, $\tilde{c}_i(\tilde{x})$, and $\tilde{g}(\tilde{x})$, $\tilde{m}_i(\tilde{x})$, and $\tilde{A}_i(\tilde{x})$ as functions of the isomorphic variable $\tilde{x}$. Following Kiselev *et al.*[26,48,57] we represent all system-dependent parameters in Eqs. (5.2)–(5.4), designated as $\tilde{k}_i(\tilde{x})$, as functions of $\tilde{x}$ and the excess critical compressibility factor $\Delta Z_c(\tilde{x})$, where

$$\Delta Z_c(\tilde{x}) = Z_c(\tilde{x}) - Z_{cid}(\tilde{x}) \tag{5.10}$$

is the difference between the actual compressibility factor of a mixture $Z_c(\tilde{x}) = P_c(\tilde{x})/R\rho_c(\tilde{x})T_c(\tilde{x})$ and its ''ideal'' part $Z_{cid}(\tilde{x}) = Z_{c1}(1-\tilde{x}) + Z_{c2}\tilde{x}$. The dimensionless coefficients $\tilde{k}$ and $\tilde{d}_1$ in this case can be written in the form[48]

$$\tilde{k}_i(\tilde{x}) = k_{i1} + (k_{i2} - k_{i1})\tilde{x} + k_i^{(1)}\Delta Z_c(\tilde{x}) + k_i^{(2)}\Delta Z_c(\tilde{x})^2, \tag{5.11}$$

and all other coefficients are given by

$$\tilde{k}_i(\tilde{x}) = \frac{P_c(\tilde{x})}{R\rho_{c1}T_{c1}}[k_{i1} + (k_{i2} - k_{i1})\tilde{x} + k_i^{(1)}\Delta Z_c(\tilde{x}) + k_i^{(2)}\Delta Z_c(\tilde{x})^2], \tag{5.12}$$

where subscripts 1 and 2 correspond to the pure D_2O and H_2O, respectively. Within the law of corresponding states (LCS), the mixing coefficients $k_i^{(j)}$ in Eqs. (5.11) and (5.12) are universal constants for all binary mixtures of simple fluids with $\Delta Z_c \leqslant 0.20$.[48]

Since the coefficients k_{i1} and k_{i2} for pure D_2O ($x=0$) and pure H_2O ($x=1$) are known, in order to specify a crossover equation of state for D_2O+H_2O mixtures one needs to know the critical locus $T_c(\tilde{x})$, $\rho_c(\tilde{x})$, and $P_c(\tilde{x})$ only. In this work, following the previous study of the D_2O+H_2O mixtures near the plait critical points,[53] for supercooled D_2O+H_2O mixtures for $T_c(\tilde{x})$ and $\rho_c(\tilde{x})$ we also use the linear expressions

$$\begin{aligned} T_c(\tilde{x}) &= T_{c1}(1-\tilde{x}) + T_{c2}\tilde{x}, \\ \rho_c(\tilde{x}) &= \rho_{c1}(1-\tilde{x}) + \rho_{c2}\tilde{x}, \end{aligned} \tag{5.13}$$

where subscripts ''$c1$'' and ''$c2$'' correspond to the critical parameters of the CP_2 in pure D_2O and H_2O, respectively. Since in this case in the entire composition range $0 < x < 1$ the difference $\Delta Z_c \ll 1$, we set the coefficients $k_i^{(2)} = 0$, and for the mixing coefficients $k_i^{(1)}$ we adopt the values originally obtained by Kiselev[26] for methane+ethane and ethane+*n*-butane mixtures. The values of these coefficients are listed in Table III. The results of our calculations of the isothermal compressibility $\kappa_{T,x}$, isobaric specific heat $C_{P,x}$, density ρ, and thermal expansivity in D_2O+H_2O mixture at equimolar composition, $x=0.5$, and atmospheric pressure, $P=0.1$ MPa, in normal and supercooled states as a function of temperature are shown in Figs. 5 and 6.

According to the principle of critical-point universality,[44–47] at fixed $\tilde{x}$ a binary mixture is isomorphic to one-component fluid. Therefore, for the calculation of the kinetic spinodal in binary mixtures one can use Eq. (2.10) but with redefined parameters $\overline{\mu}_\rho$ and $\overline{\mu}_{\rho\rho}$,

$$\begin{aligned} \overline{\mu}_\rho &= \frac{1}{k_B T}\left(\frac{\partial P}{\partial \rho}\right)_{T,\overline{x}}, \\ \overline{\mu}_{\rho\rho} &= \frac{1}{k_B T}\left[-\left(\frac{\partial P}{\partial \rho}\right)_{T,\overline{x}} + \rho\left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T,\overline{x}}\right]. \end{aligned} \tag{5.14}$$

In addition, for the heat of fusion, Δh, and specific volume, v_S, in Eq. (4.5) for D_2O+H_2O mixtures we use the simple linear approximations

$$\begin{aligned} \Delta h &= \Delta h_1(1-x) + \Delta h_2 x, \\ v_S &= v_{S1}(1-x) + v_{S2}x. \end{aligned} \tag{5.15}$$

The results of our calculations of the kinetic spinodal in pure D_2O and H_2O, and D_2O+H_2O mixture at atmospheric pressure with $\delta_T = 0$ are shown in Figs. 5 and 6. The shaded area in Figs. 5 and 6 marks the nonthermodynamic habitat calculated for the $50\%D_2O+50\%H_2O$ mixture with the CREOS-02.

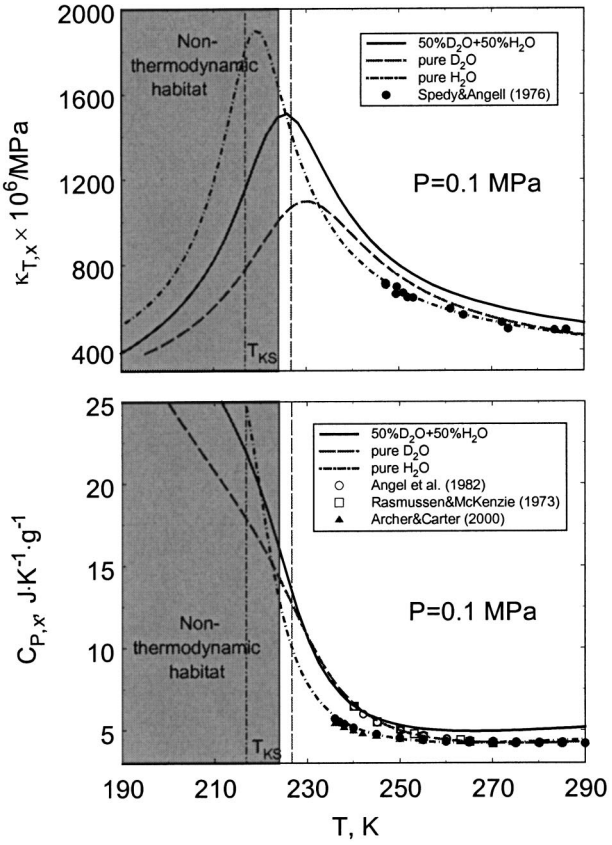

FIG. 5. The isothermal compressibility $\kappa_{T,x}$ (top) and isobaric specific heat $C_{P,x}$ (bottom) of $50\%D_2O+50\%H_2O$ mixture at atmospheric pressure, $P=0.1$ MPa, in normal and supercooled states as a function of temperature. The curves correspond to the values calculated with the CREOS-02, and the symbols represent experimental values obtained for pure D_2O (empty symbols) and pure H_2O (filled symbols) by Angell *et al.* (Refs. 36 and 61) (circles), by Archer and Carter (Ref. 62) (triangles), and by Rasmussen and MacKenzie (Ref. 37) (squares).

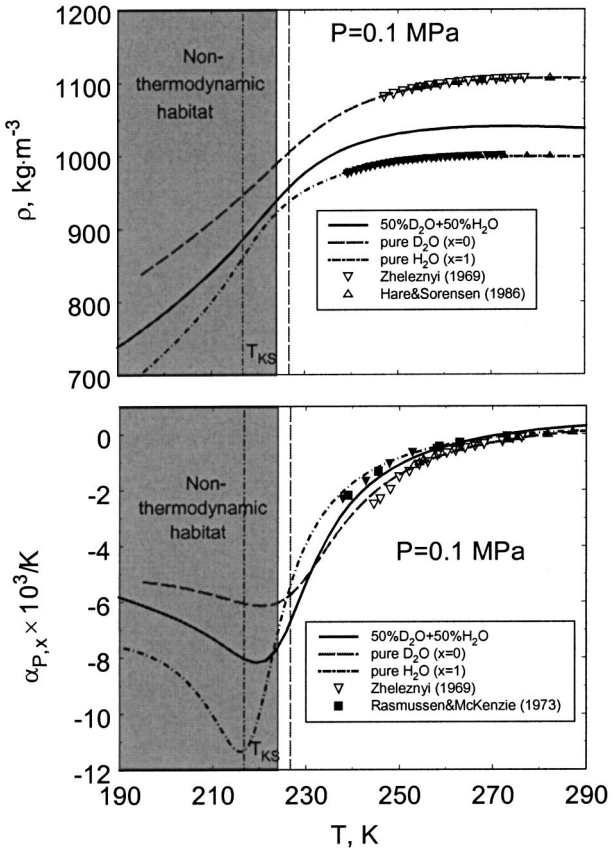

FIG. 6. The density ρ (top) and thermal expansivity (bottom) of $50\%D_2O+50\%H_2O$ mixture at atmospheric pressure, $P=0.1$ MPa, in normal and supercooled states as a function of temperature. The curves correspond to the values calculated with the CREOS-02, and the symbols represent experimental values obtained for pure D_2O (empty symbols) and pure H_2O (filled symbols) by Zheleznyi (Ref. 38) (triangles down) and by Hare and Sorensen (Ref. 40) (triangles up), and by Rasmussen and MacKenzie (Ref. 37) (squares).

VI. DISCUSSION AND SUMMARY

In the present work, we applied the fluctuation theory of homogeneous nucleation for the prediction of the kinetic spinodal in supercooled D_2O and D_2O+H_2O mixtures. In order to do this, we first developed a crossover equation of state for supercooled D_2O, CREOS-02, which predicts a second critical point, CP2, and reproduces all available experimental data in supercooled D_2O to within experimental accuracy. The kinetic spinodal, T_{KS}, calculated with the CREOS-02 lies below the homogeneous nucleation temperature, T_H, thus satisfying a physically obvious condition $T_{KS} \leqslant T_H$, and separates the statistically well-defined thermodynamic metastable states ($T_{KS} \leqslant T \leqslant T_m$) from the ''nonthermodynamic habitat'' ($T < T_{KS}$), where no thermodynamic state for supercooled D_2O is possible. We show, that similar to the CP_2 in supercooled H_2O, the CP_2 in supercooled D_2O always lies in the ''nonthermodynamic habitat'' and physically does not exist. However, the concept of the second ''virtual'' critical point is physical and extremely useful. In spite of the fact that existence of a CP_2 is prohibited by the kinetic theory, the thermodynamic surface in supercooled D_2O exhibits a nonanalytic, singular behavior caused by long-scale fluctuations in density. Similar to the system near the vapor–liquid CP_1, the intensity of these fluctuations increases as the distance to the CP_2 decreases. Physically the CP_2 can be never approached, but outside the ''nonthermodynamic habitat'' (at $T > T_{KS}$) the thermodynamic properties of the supercooled D_2O can be reproduced with high accuracy with the CREOS-02 based on the concept of this ''virtual'' critical point of HDW–LDW equilibrium.

As we discussed in Paper I, there are also other EOS and different scenarios for supercooled water. EOS such as those developed by Truskett and co-workers,[63] by Jeffery and Austin,[64] and by Ponyatovsky *et al.*[65,66] also support the two-critical point scenario and predict the existence of a second critical point in supercooled water. However, these EOS only qualitatively agree with experimental data, quantitatively the predictions of thermodynamic properties such as the isothermal compressibility, isobaric specific heat, and thermal expansivity are relatively poor, especially at high pressures.[5] The CREOS-02 yields a drastically better description of these thermodynamic properties and brings a dramatic improvement to the quantitative prediction of the two-critical point scenario. On the other hand, the singularity-free scenario[67–72] also gives a thermodynamically consistent picture of supercooled water anomalies, but without a second critical point. A simple two-state model proposed by Tanaka,[71,72] for example, also yields a reasonably good representation of the experimental data for supercooled water. Therefore, it is interesting to compare this model with CREOS-02. In Tanaka's model[71,72] all thermodynamic quantities, designated as $X(T,P)$, similar to the Eq. (3.1) for the Helmholtz free energy in CREOS-02 are also represented as a sum of the background contribution $X_B(T,P)$ and anomalous part

$$X(T,P) = X_B(T,P) + \Delta X \overline{S}, \tag{6.1}$$

where $\overline{S} = S_0 \exp[(\Delta E - \Delta v P)/k_B T]$ is so called the Boltzmann factor[72] with S_0, ΔE, and Δv as model parameters. However, the physical meaning of the background contributions in Eqs. (3.1) and (6.1) is different. In Eq. (3.1), the functions $\overline{\mu}_0(T)$ and $A_0(T)$, which correspond to the background contributions to the isochoric heat capacity $C_V = -T(\partial^2 A/\partial T^2)_V$ and pressure $P = \rho^2(\partial A/\partial \rho)_T$ along the critical isochore, respectively, are by definition smooth analytic functions of the temperature with monotonic first and second derivatives (see Fig. 7). Because of such structure of Eq. (3.1), the functions $\overline{\mu}_0(T)$ and $A_0(T)$ do not make any contributions into the singular behavior of the isothermal compressibility and thermal expansivity shown in Figs. 1 and 2. They do contribute the isobaric heat capacity through the background contribution in C_V, which in the metastable region is much smaller than C_P (see the dotted–dashed curve in Fig. 2). In the Tanaka's two-state model,[72] the background parts $X_B(T,P)$ are, in principle, unknown functions of the temperature and pressure, different for different properties. Therefore, in order to describe only the density, isothermal compressibility, and isobaric heat capacity in supercooled water as functions of temperature and pressure at least 18 adjustable parameters are needed,[72] that is approximately the same number as in the CREOS-02 (17 in the constrained model). However, even in this case the two-state model de-

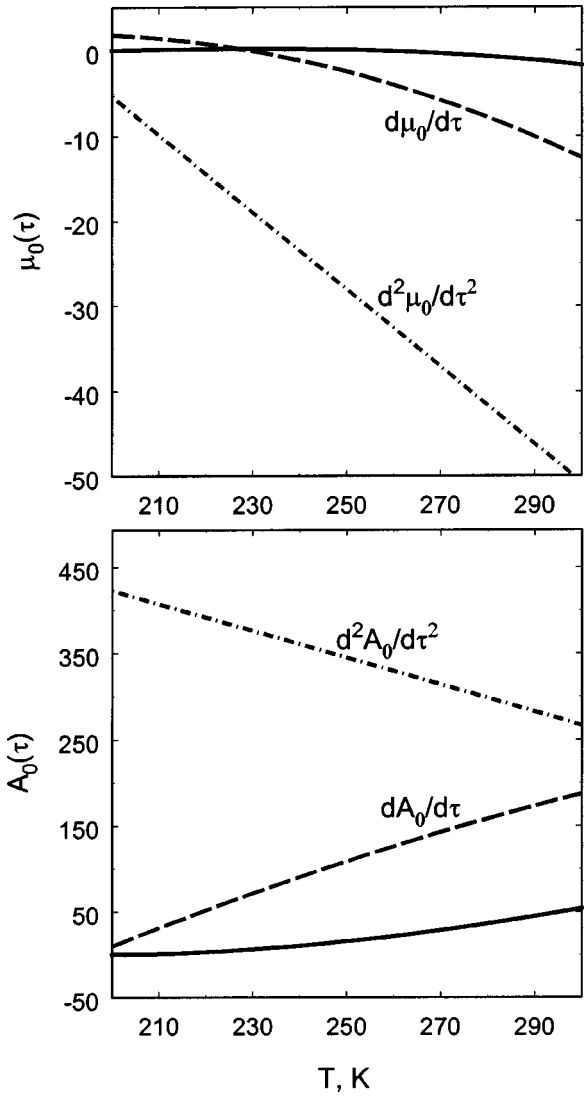

FIG. 7. The background contributions $\bar{\mu}_0(\tau)$ (top) and $\bar{A}_0(\tau)$ (bottom), and their first (dashed lines) and second (dot–dashed) lines derivatives in supercooled D_2O as functions of temperature.

veloped by Tanaka,[71,72] fails to reproduce an anomalous behavior of the isobaric heat capacity at $T<253$ K. Thus, putting away the speculations about the caloric measurements in the emulsified supercooled water,[72] we can conclude that at the present time the CREOS-02 is the only thermodynamically consistent model capable of representing the thermodynamic surface of supercooled light and heavy water within experimental accuracy and with a high degree of physical self-consistency.

We consider our results as a strong argument for the second ''virtual'' critical point scenario. However, it does not necessarily mean that the two-state model developed for supercooled water by Tanaka[71,72] should be ruled out. We believe that a combination of the ''virtual'' critical point scenario with the two-order parameter physical picture will make our model more predictive and will allow us to describe the anomalous behavior of the viscosity and diffusion coefficient in supercooled water as well as give quantitative predictions for the relaxation time t_R and glass transition temperatures. An incorporation of a second ''glass-forming'' order parameter into the CREOS-02 can be done in principle by the same way, that a dissociation–association chemical reaction in the dilute aqueous sodium chloride solutions has been incorporated into the crossover Leung–Griffiths model.[73] This study is in progress and its results will be presented in a future publication.

In the present paper, in order to test the predictability of CREOS-02, we extended the two-critical point scenario to supercooled D_2O+H_2O mixtures. Here we employed the two-critical point scenario and a principle of critical-point universality (which is successfully used for the prediction of the thermodynamic properties of binary mixtures around the locus of the plait critical points) to supercooled D_2O+H_2O mixtures, and obtained an isomorphic CREOS-02. The isomorphic CREOS-02 for supercooled D_2O+H_2O mixtures requires only the critical locus as an input and does not contain any additional adjustable parameters. Using the simple linear approximations for the ''virtual'' critical locus of HDW–LDW equilibria in supercooled D_2O+H_2O mixtures, we were able to reproduce the thermodynamic surface and the kinetic spinodal in the entire range of compositions from pure D_2O ($x=0$) to pure H_2O ($x=1$). As an example, we considered here the kinetic spinodal, T_{KS}, and the isothermal compressibility $\kappa_{T,x}$, isobaric specific heat $C_{P,x}$, density ρ, and thermal expansivity in the equimolar ($x=0.5$) D_2O+H_2O mixture at atmospheric pressure, $P=0.1$ MPa, in normal and supercooled states. Since there are no experimental data for supercooled D_2O+H_2O mixtures which could confirm or refute our calculations, we consider them as a pure theoretical prediction and a challenge to experimentalists, rather than a final physical result. In order to prove the validity of our theory for binary mixtures, more experimental measurements in supercooled D_2O+H_2O mixtures are needed.

ACKNOWLEDGMENTS

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