A NOTE ON SCENARIOS OF METASTABLE WATER

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Dedicated to Professor Ivo Nezbeda on the occasion of his 65th birthday.

A recently developed molecular-based equations of state for water are analyzed with respect to the behavior of the liquid spinodal curve. It is shown that all of them yield the spinodal exhibiting a minimum in accordance with Speedy's stability-limit conjecture and with the behavior predicted by the accurate (but purely empirical) IAPWS-95 equation. It means that the considered equations of state give consistent results but qualitatively different from those resulting from available computer simulations, which yield a monotonic spinodal line.
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The behavior of the liquid spinodal curve, i.e., the locus where liquid loses its mechanical stability, is a key feature for explaining phenomena in metastable liquid water. The core of the discussion is the concept of a retracing spinodal, which is the basic feature of Speedy's 'stability-limit conjecture'[1,2]. Speedy estimated the locus of the stability limit of liquid water by extrapolating experimental data and found that the spinodal pressure was passing through a minimum at about –200 MPa near 30 °C. He concluded that there was a single continuous line bounding the entire region of metastability including superheated, stretched, and supercooled liquid (see a sketch in Fig. 1). Apparent divergence of response functions in the vicinity of limits of supercooling was then attributed to approaching the spinodal locus.

Deeply metastable regions of water are experimentally accessible only with great difficulties. An indirect experimental source of information about limits of stability of stretched and superheated liquid are cavitation

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experiments[3,4]. In contrast to spinodal instability, cavitation is a kinetically driven phenomenon and its onset depends on the experimental setup (the same applies for nucleation of liquid from vapor). The spinodal itself is an ultimate boundary of the metastable region and no experimentally measurable limit of stability, including the cavitation pressure, can reach it. Whether it can be approached close enough to enable to draw unbiased conclusions about its behavior remains still unclear. Consequently, interpretation of the cavitation measurements in terms of the shape of the liquid spinodal remains thus indefinite. For a discussion on kinetic limits of stability see a series of papers by Kiselev[5–7].

There are empirical (but extremely accurate) equations of state (EOS's) developed for industrial purposes by fitting a huge body of available experimental data on water. The one highly recommended and most frequently employed is the IAPWS-95 equation[8]. When this equation is used in the metastable region, it yields a retracing spinodal curve providing thus support for Speedy's scenario. Figure 7.54 in ref.[8] shows the IAPWS-95 spinodal along with those calculated from two older empirical equations; they all retrace. However, with respect to a purely empirical form of the considered EOS's, any extrapolation must be taken with caution.

In computational studies, attempts to access metastable parts of water phase diagram have been made by means of molecular simulation on realistic models. There are results available for ST2 [9–12], TIP4P [10,13], SPC/E [14,15], TIP5P [16] and polarizable[17] models of water. All of the simulation studies

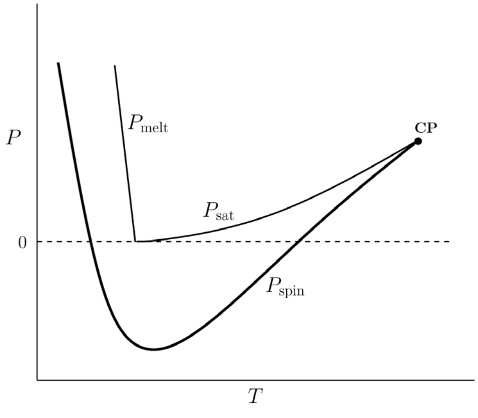

FIG. 1
A schematic picture of Speedy's stability-limit conjecture[1,2]. P_{spin} stands for the spinodal line, P_{sat} is the saturated-vapor line (boiling point), P_{melt} indicates the melting line, and CP stands for the vapor–liquid critical point

cited above exhibit a non-retracing, monotonic spinodal in contrast to Speedy's conjecture. Instead, they suggest the occurrence of the liquid–liquid critical point, introduced by Poole et al.[9], accounting for the behavior of response functions in supercooled region. Available simulation studies on the liquid–liquid transition in water were summarized by Brovchenko and Oleinikova[18].

Apart from 'realistic' simulations, calculations have been performed on simplified models capturing the essence of water's bonding properties. Studies on lattice models exhibit the spinodal curve with a minimum[19,20] or a so-called singularity-free scenario[21]. Poole et al.[22] proposed an extension of the van der Waals equation which incorporates hydrogen bonding. This equation yields the liquid–liquid critical point. When the bonding energy decreases under certain threshold, the liquid–liquid critical point enters the unstable part of the isotherm resulting in the retracing spinodal curve, suggesting that the two scenarios "may be fundamentally related". There is a similar work of Truskett et al.[23], where an analytical equation of state yields either the liquid–liquid critical point or the singularity-free scenario depending on geometric parameters of bonding. For a review of theories of metastable water, we refer the reader to the paper by Debenedetti[24].

As one can see above, there are several groups of methods attempting to reveal the nature of stability limits of liquid water; nevertheless, there is no consensus among them. Moreover, each of the above-described method seems to suffer from some inherent defects. The spinodal curve is, in principle, directly unreachable both from experiment and conventional simulations and must be obtained by extrapolation or by special methods. Concerning EOS's, here the spinodal results from their unphysical continuous behavior throughout the entire temperature–density plane and need not thus represent the actual limit of stability. In the case of molecular simulation, the inability of the conventional *NVT* ensemble to correctly maintain liquid–vapor metastability appears to discard 'spinodals' determined by molecular simulations; an exception is the work of Brovchenko et al.[11], who employ a restricted *NPT* ensemble ensuring homogeneity of the fluid in the simulation box. Other authors cited above wrongly attributed the simulated 'finite-size' loops, which are actually stable, to metastable and unstable portions of the true van der Waals loops, extrema of which constitute spinodals. The above-described feature of the constant-volume simulation has been known[25,26] for a long time and it has been pointed out again recently on several occasions[18,27–29].

Within the development of a molecular theory of polar and associating fluids, Nezbeda and Weingerl[30] proposed some time ago a semi-theoretical

EOS for water. The equation is based on a perturbation expansion about a short-range reference and its parameters were obtained by fitting to the experimental vapor–liquid equilibrium data. The equation (further referred to as the NW equation) performs very well over a wide range of temperatures and densities, and, with respect to its sound theoretical footing, its extension to the metastable region may be less questionable than in the case of purely empirical EOS's. A similar procedure has been used by the present authors to develop another semi-theoretical EOS [31] based on the TIP4P water model[32].

Following research along the same line we have recently developed a sort of a 'first-principle' EOS [33]. The equation results from a purely theoretical treatment using the intermolecular interaction potential obtained, by well-defined approximations, from a realistic parent model (TIP4P water) as the only input and applying Wertheim's thermodynamic perturbation theory[34,35] of the 2nd order[36]. This EOS produces all interesting anomalies observed on real water, including the temperature of maximum density (TMD) and its shift towards lower temperatures upon compression. But, what is even more important is the fact that this EOS is free of any additional fitting to experimental data and removes thus one uncertainty inherent to the empirical and semi-empirical EOS's adjusted to experiment: unreliable extrapolation.

With all these appealing features of the aforementioned EOS's, it is tempting to use them also in the metastable range and to contribute to yet unresolved controversies as for the behavior of the spinodal. In the next section Theory we present, in a concise form, the considered EOS's, and in Results and Discussion we show and discuss the features of the obtained spinodal. Conclusions are then summarized in the last section.

THEORY

In terms of an analytical equation of state, the liquid spinodal curve can be defined as a set of points where the relations

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \tag{1}$$

and

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T > 0 \tag{2}$$

are satisfied. In the above expressions P is the pressure, V the volume, and T the temperature.

A general molecular-based approach to obtain an EOS in an analytic form is via a perturbation expansion[37]. It means, the given interaction potential, u, is split into a short-range reference part, u_{ref}, and a perturbation part, the latter having a negligible effect on the structure[38] of the fluid. The corresponding EOS assumes thus the form

$$z = z_{\mathrm{ref}} + \Delta z \tag{3}$$

where z is the compressibility factor, $z = \beta P/\rho$, $\beta = 1/k_{\mathrm{B}}T$, k_{B} is the Boltzmann constant and ρ is the number density. The short-range part includes both repulsive and attractive interactions[39], and, in the case of polar and associating fluids, like water, it captures also a good deal of the thermodynamic properties of the system at hand[40–42]. It is thus reasonable to write, at the zeroth level of approximation,

$$z \approx z_{\mathrm{ref}} \,. \tag{4}$$

When dealing with water, the total potential u is given by non-electrostatic interactions, typically the Lennard–Jones (LJ) located at the oxygen atom, and electrostatic interactions between certain Coulombic sites. The corresponding short-range reference, u_{ref}, incorporating both these types of interactions is still too complex for its properties to be estimated directly. It is therefore mapped onto the so-called primitive model (PM)[43,44] so that Eq. (3) becomes

$$z = z_{\mathrm{PM}} + \Delta z \,. \tag{5}$$

The PM copies the geometry of the realistic parent model and approximates the realistic force field by hard-sphere (HS) and square-well (SW) interactions to mimic repulsive and attractive forces between the sites, respectively. The complete intermolecular interaction energy of such a PM assumes then the form

$$u_{\mathrm{PM}}(\mathbf{1},\mathbf{2}) = u_{\mathrm{HS}}(r_{\mathrm{OO}};d_{\mathrm{OO}}) + \sum_{\substack{ij\in\{\mathrm{XX}\}\\ ij\in\{\mathrm{YY}\}}} u_{\mathrm{HS}}(r_{ij};d_{ij}) + \sum_{ij\in\{\mathrm{XY}\}} u_{\mathrm{SW}}(r_{ij};\lambda) \tag{6}$$

where (**1**,**2**) is the short-hand notation for the dependence of u on both the position and orientation of molecules 1 and 2, d_{OO} is the diameter of an oxygen-centered hard sphere representing a radially symmetric component of repulsive forces, r_{ij} is the distance between site i on molecule 1 and site j on molecule 2, and X and Y symbolize 'positive' and 'negative' Coulombic-like sites, respectively. The summation in the second term on the right-hand side of Eq. (*6*) runs over the pairs of like sites and that in the third term over the pairs of unlike sites. Further,

$$\begin{aligned} u_{HS}(r;d) &= +\infty \quad \text{for} \quad r < d \\ u_{HS}(r;d) &= 0 \quad \text{for} \quad r > d \end{aligned} \qquad (7)$$

and

$$\begin{aligned} u_{SW}(r;\lambda) &= -\varepsilon_{HB} \quad \text{for} \quad r < \lambda \\ u_{SW}(r;\lambda) &= 0 \quad \text{for} \quad r > \lambda \end{aligned} \qquad (8)$$

are the hard-sphere and the square-well interactions, respectively. The first two repulsive terms on the right-hand side of Eq. (*6*) together define a pseudo-hard body (PHB)[45]. For further details on the PM we refer the reader to the original papers[43,44].

The theoretical basis of EOS's for associating fluids is the Wertheim thermodynamic perturbation theory (TPT)[34–36] used either in the first (TPT1) or second (TPT2) order to derive an EOS for the reference term, the primitive model. Nezbeda and Weingerl[30] derived a semi-theoretical EOS in the form (*3*) using only the functional form of the TPT1 and adjusted all its parameters to experimental data. The perturbation term was given by

$$\Delta z = z_{disp} + z_{DD} \qquad (9)$$

where for the contribution of the dispersion and dipole–dipole interactions, z_{disp} and z_{DD}, respectively, they used the simplest expressions available with parameters adjusted, again, to experimental data. For the explicit EOS formula and its parameters we refer the reader to the original paper[30].

Another attempt to derive a theoretically-footed EOS for water was made by Jirsák and Nezbeda[31]. They followed the same procedure as that used in the development of the NW equation, except for the reference term, which was derived within the TPT2, and they fitted the equation to simulation data for TIP4P water. The resulting EOS reproduces the location of the temperature of maximum density for the considered water model. See the original paper[31] for details.

As an attempt to derive a truly theoretical EOS, i.e., to start from a given Hamiltonian and to avoid resorting to any experimental data, Jirsák and Nezbeda[33] have considered recently an EOS in the form (*4*) and used the TPT2 for the PM descending from the TIP4P potential. Within the TPT2, the compressibility factor of the PM is given by

$$z_{\mathrm{PM}} = z_{\mathrm{PHB}} + \rho^* \left(\frac{\partial}{\partial \rho^*} [m(1-\nu) + \ln x_0] \right)_\beta \qquad (10)$$

where z_{PHB} is the compressibility factor of the underlying PHB fluid, $\rho^* = \rho d_{\mathrm{OO}}^3$ is the reduced number density, and the two terms in the derivative account for hydrogen bonding mimicked by the SW attraction. Here d_{OO} is temperature dependent, in contrast to ref.[31]. The compressibility factor of PHB's is known in a parametrized form,

$$z_{\mathrm{PHB}} = \frac{1 + \alpha_1 \eta + \alpha_2 \eta^2 - \alpha_3 \eta^3}{(1-\eta)^3} \qquad (11)$$

where $\eta = (\pi/6)\rho^*$ denotes the packing fraction and α_i are numerical constants given for the considered models in ref.[46]. For x_0, we use the expression

$$x_0 = \frac{\nu^m}{[1 + m\rho^*\nu I_{+-} + (m\rho^*\nu)^2 I_{+-+}]^n} \qquad (12)$$

and ν satisfies the cubic equation

$$\begin{gathered} m^2 \rho^{*2} I_{+-+} \nu^3 + [(2mn - m^2)\rho^{*2} I_{+-+} + m\rho^* I_{+-}]\nu^2 + \\ + [(n-m)\rho^* I_{+-} + 1]\nu - 1 = 0 . \end{gathered} \qquad (13)$$

Integers m and n stand for the number of sites X and Y, respectively; for the PM descending from the TIP4P potential, PM/TIP4P, $m = 2$ and $n = 1$. Quantities I_{+-} and I_{+-+} are fundamental integrals of the TPT2; see ref.[36] for details.

RESULTS AND DISCUSSION

First we present scenarios calculated using the two semi-theoretical EOS's that consist of both the reference and perturbation terms. In Fig. 2 we plot the calculated spinodal line, saturated-vapor pressure, and the locus of the TMD for the NW EOS [30], i.e., the full equation of state for real water. As can be seen, the spinodal line exhibits a minimum – at the point where it also meets the TMD line, as required by thermodynamics[1,2]. Figure 3 shows then results calculated using the TPT2-based equation of state[31] for the TIP4P model of water. The situation is quite similar to that for the NW equation, but here the TMD line crosses the melting line, as it should.

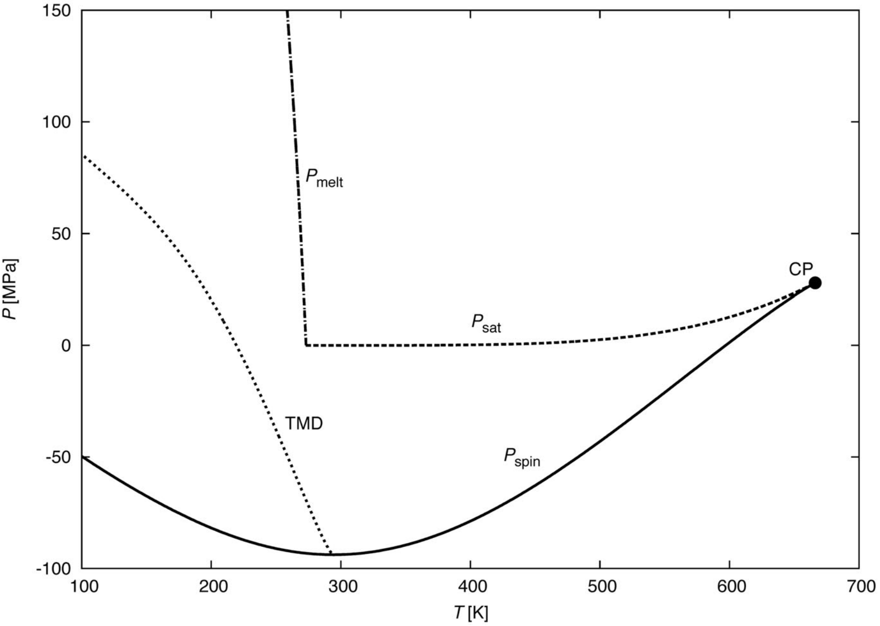

FIG. 2

Scenario for the EOS of Nezbeda and Weingerl[30]. Dashed line (P_{sat}) represents the saturated-vapor pressure, dotted line (TMD) demarcates the locus of density maxima, and full line (P_{spin}) is the liquid spinodal. The vapor–liquid critical point (CP) is indicated by a circle. Dash-dotted melting line (P_{melt}) is calculated from the equation[48] parametrizing experimental data for real water

As it has been already mentioned, the short-range reference system captures completely the structure of the full parent system and also a good deal of its thermodynamics. In a recent study[33], we have thus analyzed the behavior of water resulting only from the appropriately-defined primitive model and we apply this approach also in the present paper to study metastable water. First, we use this EOS in a straightforward restricted version with the HS diameter, d_{OO}, set to a fixed value determined from the parent potential model at the ambient temperature – this is the approach usually used for PM references. Finally, we employ an unrestricted version, in which also the diameter d_{OO} is subject to the perturbation treatment, as it should be, which results then in its temperature dependence. This theoretically-footed temperature dependence of the diameter distinguishes our recently developed approach[33] from older studies.

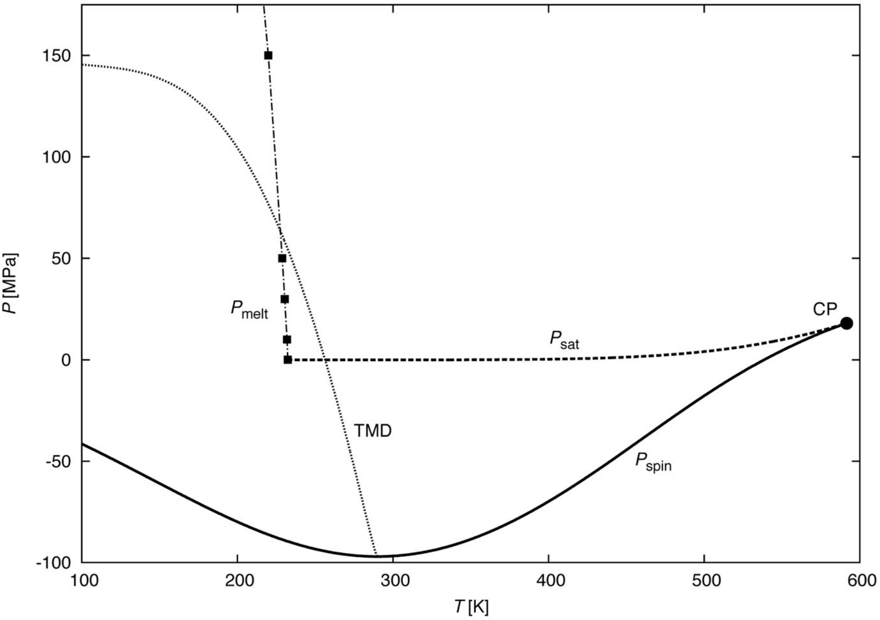

FIG. 3
Scenario for the TIP4P EOS of Jirsák and Nezbeda[31]. Dashed line (P_{sat}) represents the saturated-vapor pressure, dotted line (TMD) demarcates the locus of density maxima, and full line (P_{spin}) is the liquid spinodal. The vapor–liquid critical point (CP) is indicated by a circle. Black squares are the melting points of the TIP4P model of water determined by molecular simulation[49]; the dash-dotted line is drawn to guide the eyes

Results of the two mentioned versions of the theoretical EOS are given in Figs 4 and 5 and both exhibit a minimum on the spinodal curve. There are, however, minor differences in both scenarios. Temperature dependence of d_{OO} not only brings the density maximum above the zero pressure but also adds a new feature – a line of density minimum, which ends at a common point with the line of density maximum (this is necessary for an analytic density); see Fig. 5. It is worth noting that the value $\varepsilon/k_B = 4123$ K used in Figs 4 and 5 reproduces correctly the location of the TMD of the TIP4P model, –15 °C at 1 bar (ref.[47]), when used in the equation with the temperature-dependent diameter (Fig. 5).

As we have seen, all the presented perturbation equations of state yield a minimum on the spinodal curve. Nonetheless, one can notice that they do not retrace, in contrast to Speedy's stability-limit conjecture[1,2], to positive pressures. A similar behavior of the spinodal curve is observed also in some lattice models[19,20,24]. As regards the possibility of the liquid–liquid transition, no indication of another critical point has been found so far on isotherms predicted by the presented equations.

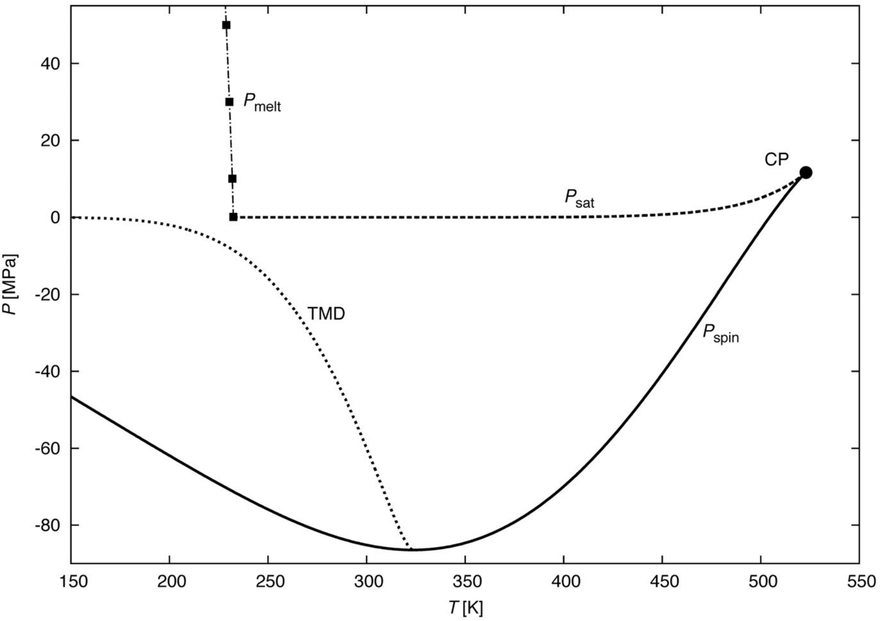

FIG. 4
Scenario for PM/TIP4P with a fixed diameter (d_{OO} = 2.652 Å, ε/k_B = 4123 K; other parameters taken from ref.[44]). Symbols and lines have the same meaning as in Fig. 3

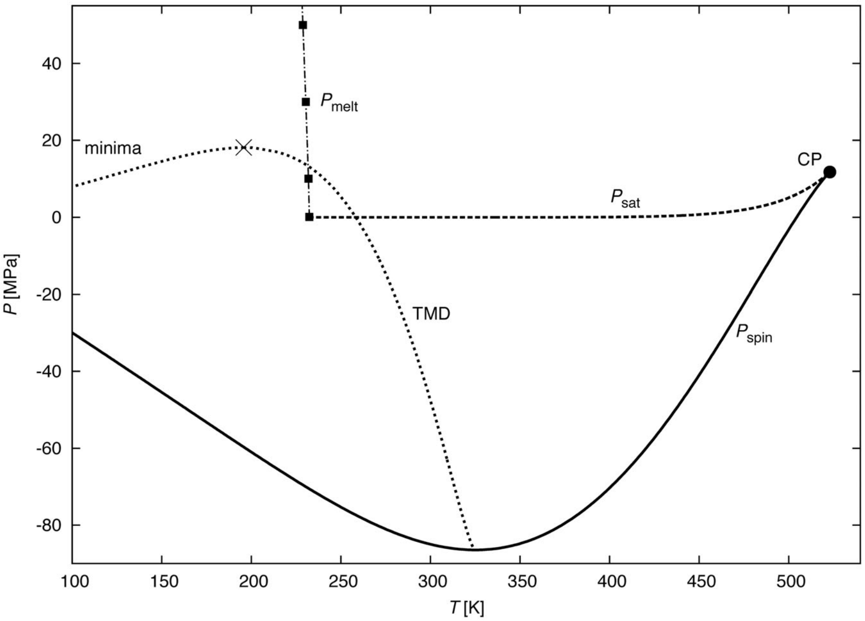

FIG. 5
Scenario for PM/TIP4P with temperature-dependent diameter $d_{\text{OO}}{}^{33}$ (ε/k_{B} = 4123 K). The legend is the same as in Fig. 3, plus there is an additional dotted line of density minima that meets the TMD line at the point indicated by a cross

CONCLUSIONS

Whether the liquid spinodal of water is retracing or not is still a matter of controversy. On one hand, empirical parametrizations of *PVT* data of real water, as well as certain class of molecular-based equations of state, extrapolate to a retracing spinodal. On the other hand, spinodals obtained by molecular simulations exhibit a monotonic trend. Considerations of this matter should always take account of the fact that there is no direct experimental method making it possible to determine the actual spinodal, i.e., the line where conditions (*1*) and (*2*) hold true. One can obtain either extrapolation or a kinetic limit of stability preceding the mechanical one. As regards the theoretical calculations, one is always limited by the method (involving necessary approximations) and by the appropriateness of the model employed.

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