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Free energy surface of supercooled water

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We present a detailed analysis of the free energy surface of a well characterized rigid model for water in supercooled states. We propose a functional form for the liquid free energy, supported by recent theoretical predictions [Y. Rosenfeld and P. Tarazona, Mol. Phys. **95**, 141 (1998)], and use it to locate the position of a liquid-liquid critical point at $T_{C'}=130\pm 5$ K, $P_{C'}=290\pm 30$ MPa, and $\rho_{C'}=1.10\pm 0.03$ g/cm^3. The observation of the critical point strengthens the possibility that the extended simple point charge model of water may undergo a liquid-liquid phase transition. Finally, we discuss the possibility that the approach to the liquid-liquid critical point could be pre-empted by the glass transition.

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I. INTRODUCTION

The thermodynamic description of supercooled water has been a major research topic in recent years. Striking anomalies—such as the existence of a minimum in the isothermal compressibility K_T along isobars, the increase of the isobaric specific heat C_P on cooling, and the temperature of maximum density T_{MD} along isobars—characterize the behavior of liquid water [1–3]. In particular, the study of supercooled states of water sheds light on the understanding of the anomalous behavior of liquid water. The increase of K_T and C_p on supercooling reinforces the possibility that the thermodynamic properties of supercooled water could be different from those of simple liquids. Speedy and Angell proposed a scenario in which the increase of K_T and C_p is related to a reentrant spinodal line in the phase diagram of water by postulating the existence of an ultimate limit of stability for the liquid phase on cooling [4].

More recently, increased computing power has made possible the numerical study of the thermodynamic properties of models for water. In particular, supercooled states, where relaxation times increase by several orders of magnitude over typical liquid values, have become computationally accessible. It has been shown that explicit atom models (such as ST2 [5], TIP4P/TIP5P [6], and SPC/E [7]), as well as lattice [8] and continuum [9] models, are able to reproduce the anomalous thermodynamic properties of water. In all the atomistic models that have been studied, it has been found that the spinodal line is *not* reentrant. Additionally, for the ST2 model, the existence of a novel liquid-liquid critical point has been directly observed in molecular dynamics simulations [10]. Hence, it has been proposed that the anomalous thermodynamic properties of liquid water could be related to a liquid-liquid phase transition. According to this hypothesis, two distinct forms of liquid water, separated by a first-order transition, may exist below a critical temperature T_c; such a critical point would account for the unusual increases in the thermodynamic response functions on cooling. Unfortunately, in water, the estimated T_c is below the homogeneous nucleation temperature, i.e., inside the so-called ''no-man's land.'' This notwithstanding, recent experiments [11] have probed the possible thermodynamic scenarios which characterize liquid water [3,4,10,12].

From a simulation point of view, the ST2 model is the only one that allows a direct study of the liquid-liquid critical point; an increase of many orders of magnitude in computing power is needed for a direct detection of a critical point in other point charge models. Also, in supercooled states at the same T and P, ST2 molecules are more mobile compared to real water. This feature has been exploited for equilibrating configurations at relatively low T [10,13]. The ST2 potential is *overstructured* compared to water, and the equation of state is shifted to higher values of pressure P and temperature T [10].

Among the molecular potentials that have been studied in detail, a significant role has been played by the extended simple point charge (SPC/E) model, both because of its simplicity and its success in capturing the properties of water in the bulk state [14–17], as well as in biological systems [18]. The SPC/E model has three point charges, located at the atomic centers of the water molecule. SPC/E is *understructured*, with its equation of states shifted to lower values of P and T compared to water [14]. Also, in the supercooled regime, at the same T and P, SPC/E molecules are less mobile than real water molecules [15–17]. Since it has been shown that the ST2 and SPC/E models bracket the thermodynamic behavior of water in the T-P plane [14], it would be encouraging to clearly detect the presence of a liquid-liquid critical point also in the SPC/E potential. Unfortunately, the reduced diffusivity of SPC/E compared to ST2 makes it impossible to study directly the low T and high P region, where the SPC/E second critical point should be located.

Here we propose a functional form for the free energy surface of the SPC/E model in the low temperature region. Our work is supported by recent theoretical predictions for the T dependence of the potential energy in supercooled

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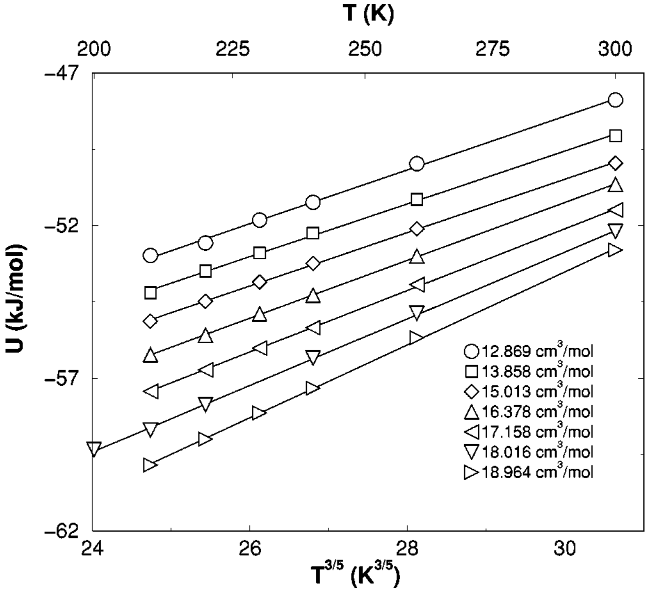

FIG. 1. Fit of the potential energy along isochores with the functional form $U_0+\alpha T^{3/5}$. Symbols denote different molar volumes. For the sake of clarity, the different isochores are shifted by -1 kJ/mol each in order to avoid overlaps.

states [19], which have been tested for several model liquids [20–24]. The calculated functional form provides a good description of the thermodynamic quantities in the region where simulations are feasible, and predicts the presence of a liquid-liquid critical point C' at $T_{C'}=130\pm5$ K, $P_{C'}=290\pm30$ MPa, and $\rho_{C'}=1.10\pm0.03$ g/cm^3, in reasonable agreement with prior estimates [14] based on the characteristic shift in thermodynamics properties between the SPC/E and the ST2 model.

II. THE SPC/E HELMHOLTZ FREE ENERGY

The numerical data used to calculate the Helmholtz free energy $F=E-TS$ are obtained from the long molecular dynamics simulations of Ref. [16] for 42 different state points, comprising seven different densities and six different temperatures. The simulation results for the total energy E and pressure P are used here to reconstruct F in the region $T>210$ K, as we describe below. As noted in Ref. [14], the energy E as a function of V develops an increasingly pronounced convexity on lowering T. This signals the possibility of a phase transition, as $F=E-TS$ will be then also convex at low T.

Simulations of the SPC/E model below $T\approx200$ K are not feasible at the present time, as the time needed to observe equilibrium metastable properties exceeds currently available resources. Here, the simulation data for SPC/E water are limited to the region $T>200$ K. To investigate the phase behavior at lower T, we exploit the recently proposed relationship for the low-T dependence of the potential energy U along isochoric paths [19]. Specifically, the low-T behavior of the potential energy is predicted to follow the functional form [19]

$$U_{\rm fit}(T,V)=U_0(V)+\alpha(V)T^{3/5}. \tag{1}$$

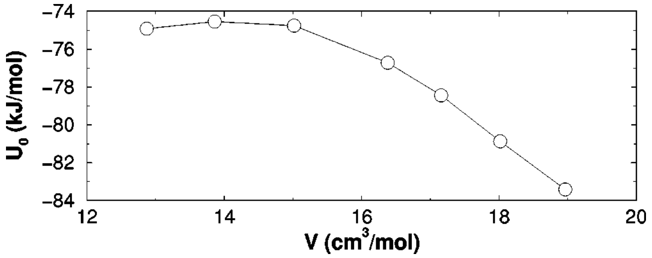

FIG. 2. Volume dependence of $U_0(V)$ from Eq. (2). Note that this coincides with $F(T=0\text{ K},V)$. The negative curvature implies the presence of an unstable region in the phase diagram at low T.

Here U_0 represents the $T=0$ K value of $U_{\rm fit}$, which for a classical system may also be identified with $F(0,V)$. The functional form of Eq. (1) has been shown to describe the temperature dependence of the potential energy in several different models, ranging from Lennard-Jones to Yukawa potentials [20,21,23,24]. Although no specific prediction has been presented until now for molecular systems, we find that in the temperature range between $T=200$ and 300 K the SPC/E potential energy is very well described by the $T^{3/5}$ law, as shown in Fig. 1. The volume dependence of $U_0(V)$ and $\alpha(V)$ are reported in Fig. 2 and in Table I. Since $F(T=0,V)$ coincides with $U_0(V)$, the clear negative concavity of $U_0(V)$ at large volumes indicates that if the $T^{3/5}$ law would hold down to $T=0$ K, then the extrapolated liquid free energy would imply a two-phase coexistence at zero temperature. As will be discussed in more detail later, at $T=0$ K the two phases are separated by a first-order transition around $P=380$ MPa.

Since the V dependence of U_0 and α is smooth, we derive a functional form $U_{\rm fit}(V,T)$, by fitting the values of $U_0(V)$ and $\alpha(V)$ with sixth degree polynomials $U_0(V)=\Sigma_{n=0}^{6}b_nV^n$ and $\alpha(V)=\Sigma_{n=0}^{6}a_nV^n$. We thus obtain

$$U_{\rm fit}(T,V)=\sum_{n=0}^{6}a_nV^n+T^{3/5}\sum_{n=0}^{6}b_nV^n. \tag{2}$$

The a_n and b_n values are reported in Table II. We find almost identical values of U_0 and α if we truncate Eq. (2) at order V^5. The resulting expression $E(V,T)=3k_BT+U_{\rm fit}(V,T)$ for the total energy describes very well the simulation results, as shown in Fig. 3.

We obtain the entropy S using the thermodynamic relation

TABLE I. Fitting parameters for the potential energy to Eq. (1). The fits are made for 210 K≤T≤300 K.

V (cm^3/mol)	U_0 (kJ/mol)	α [kJ/(mol K$^{3/5}$)]
18.96421	−83.41894	1.1970260
18.01600	−80.86653	1.1000960
17.15810	−78.47431	1.0130790
16.37818	−76.65199	0.9468765
15.01333	−74.77946	0.8767148
13.85846	−74.50920	0.8653371
12.86857	−74.91184	0.8835562

TABLE II. Polynomial fitting coefficients for $U_0(V)$, $\alpha(V)$ [see Eq. (2)], and for $P(T=300\ \mathrm{K},V)$ [Eq. 5]. Note that the dimensions of the coefficients depend on the term n of the expansion.

n	a_n (kJ mol^{n-1}/cm^{3n})	b_n (kJ mol^{n-1}/(K$^{3/5}$ cm^{3n})	c_n (MPa mol^{n}/cm^{3n})
0	76.617	-1.8261	6.8671×10^{4}
1	-30.435	0.61927	2.4466×10^{3}
2	1.279.8	-2.9301×10^{-2}	2.8096×10^{3}
3	5.0719×10^{-2}	-9.6397×10^{-4}	3.0755×10^{2}
4	4.4964×10^{-5}	-2.63884×10^{-5}	1.2970×10^{1}
5	-3.7530×10^{-4}	1.07393×10^{-5}	0.1871
6	1.1301×10^{-5}	-3.1252×10^{-7}	3.4974×10^{-4}

$$S(T,V)=S(T_0,V_0)+\frac{1}{T}\int_{T_0,V_0}^{T,V}(dE+PdV) \tag{3}$$

where the state point (T_0,V_0) is some reference state point. We calculate the temperature dependence of S along isochores from Eq. (2) by performing thermodynamic integration along constant V paths. $S(T,V)$ is given by

$$\begin{aligned}S(T,V)&=S(T_0,V)+\int_{T_0}^{T}\frac{dT}{T}\left(\frac{\partial E}{\partial T}\right)_V\\&=S(T_0,V)+3k_B\ln\left(\frac{T}{T_0}\right)-\frac{3}{2}\alpha(V)(T^{-2/5}-T_0^{-2/5}).\end{aligned} \tag{4}$$

The unknown $S(T_0,V)$ function can be evaluated, at any chosen T_0, from the knowledge of the V dependence of P using Eq. (3). To calculate $S(T_0,V)$ we fit the simulation data for $P(T=300\ \mathrm{K},V)$ again with a sixth-order polynomial

$$P_{\mathrm{fit}}(T=300\ \ \mathrm{K},V)=\sum_{n=0}^{6}c_nV^n. \tag{5}$$

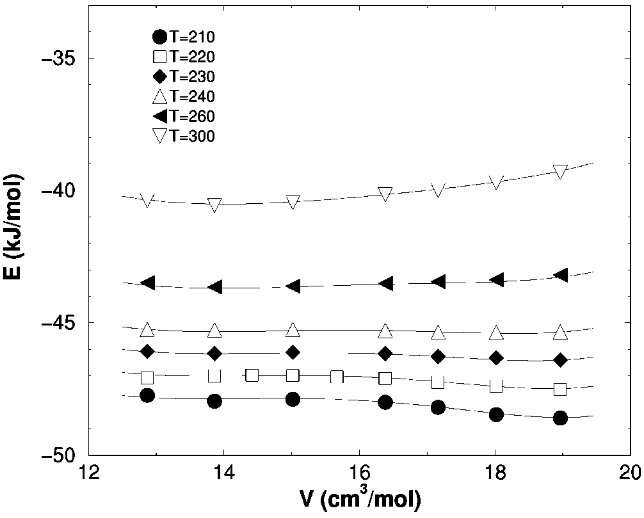

FIG. 3. Comparison between the energy E calculated from simulations [14] (symbols) and from the free energy approach described here (continuous lines).

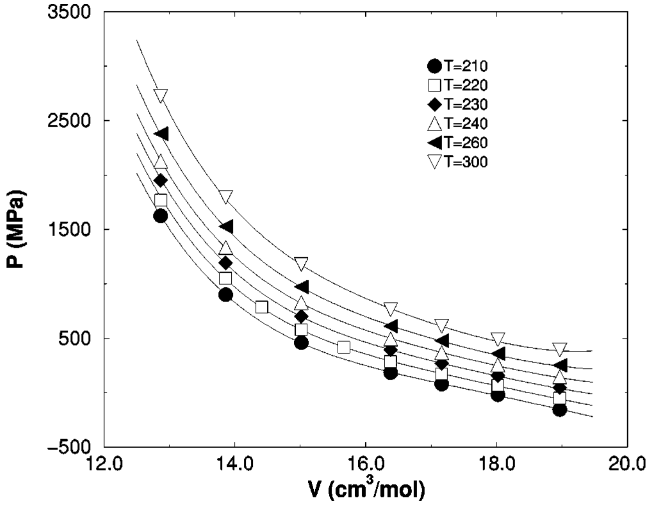

FIG. 4. Comparison between pressures as calculated from Fig. 3.

The values of the resulting c_n coefficients are reported in Table II. From elementary calculus,

$$\begin{aligned}S(T_0,V)=S(T_0,V_0)-&\frac{E(T_0,V_0)-E(T_0,V)}{T_0}\\&+\sum_{n=0}^{6}\frac{c_n}{n+1}\frac{V^{n+1}-V_0^{n+1}}{T_0}.\end{aligned} \tag{6}$$

The only unknown quantity left is $F(T_0,V_0)$, which can be calculated, if needed, starting from a known reference point (as, for example, an ideal gas state, as done in Ref. [21]) and performing thermodynamic integration up to V_0,T_0. The resulting expression for $F(T,V)=E(T,V)-TS(T,V)$ can then be used to calculate thermodynamic properties of SPC/E water.

III. RESULTS

First, we compare in Figs. 3 and 4 the values of $E_{\mathrm{fit}}=(1-T\partial/\partial T)F_{\mathrm{fit}}$ and $P_{\mathrm{fit}}=-\partial F_{\mathrm{fit}}/\partial V$ with the simulation results for $T<300$ K. Note that the derivatives eliminate the unknown constant $F(V_0,T_0)$. We also calculate the line of density maxima, T_{MD}, defined as the locus where $(\partial V/\partial T)_P=0$. The predicted line is compared with the results of the simulations in Fig. 6.

We next use the expression for F to calculate the thermodynamic properties for $T<200$ K where simulations are not feasible. The free energy expression proposed depends primarily on the assumption of the $T^{3/5}$ dependence of the potential energy in supercooled states. The theoretical prediction and the quality of the $T^{3/5}$ description reported in Fig. 1 suggests that we may meaningfully extrapolate the calculation to a temperature lower than the one for which equilibration is feasible at the present time, and search for the possibility of a liquid-liquid critical point.

We calculate P_{fit} and find that, at temperatures lower than 130 ± 5 K, a van der Waals loop (Fig. 5) develops, signaling a first-order transition between two liquid phases. The common tangent construction [25] for the Helmholtz free energy F_{fit} allows us to calculate the coexistence line; further, we

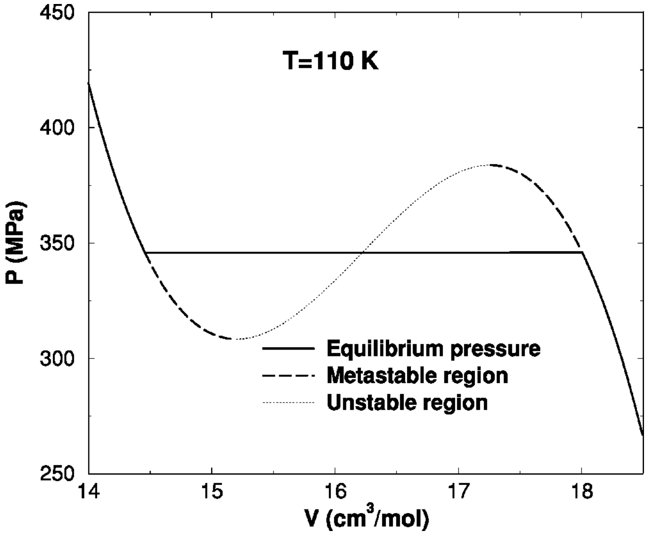

FIG. 5. Pressure at $T=100$ K as calculated. The equilibrium pressure is obtained by the Maxwell construction.

calculate the spinodal lines $(\partial P_{\rm fit}/\partial V)_T=0$. The coexistence line meets the spinodal at a critical point C', which we find at $T_{C'}=130\pm5$ K, $P_{C'}=290\pm30$ MPa, and $\rho_{C'}=1.10\pm0.03$ g/cm^3.

The resulting SPC/E phase diagram is shown in Fig. 6 in both the $(P-T)$ and $(\rho-T)$ planes. Figure 6 also shows the recently-calculated Kauzmann temperature T_K locus [21], defined as the temperature at which the configurational entropy vanishes [26]. The evaluation of the Kauzmann locus is also based on the assumption that the system potential energy has a $T^{3/5}$ dependence, and hence is fully consistent with the present free energy calculations. We note that the predicted critical temperature is ≈10 K below the Kauzmann temperature where SPC/E water is predicted to have a vanishing diffusivity [21].

As a final consideration, we discuss the interplay between the location of the critical point and the Kauzmann line. Since at the Kauzmann line the configurational entropy vanishes, all equilibrium thermodynamic calculations lose meaning below this line. In this sense, the critical point in the SPC/E phase diagram should not be considered. In the potential energy landscape paradigm [26–29], the system would be trapped in a single basin reached at T_K. Nonetheless, the free energy below T_K can still be calculated by considering its separate parts. The contribution to the free energy due to the multiplicity of basins sampled would be fixed at its value at T_K, i.e., zero. Thus, below T_K the intrabasin free energy coincides with F. At low T, frequently, a model based on a harmonic solid is appropriate for such a calculation [20–22]. The free energy calculated will still display a critical point (but slightly shifted compared to the present estimate) since the basic mechanism which gives rise to the low-T instability is the shape of $E(V,T)$, which is already convex well above T_K.

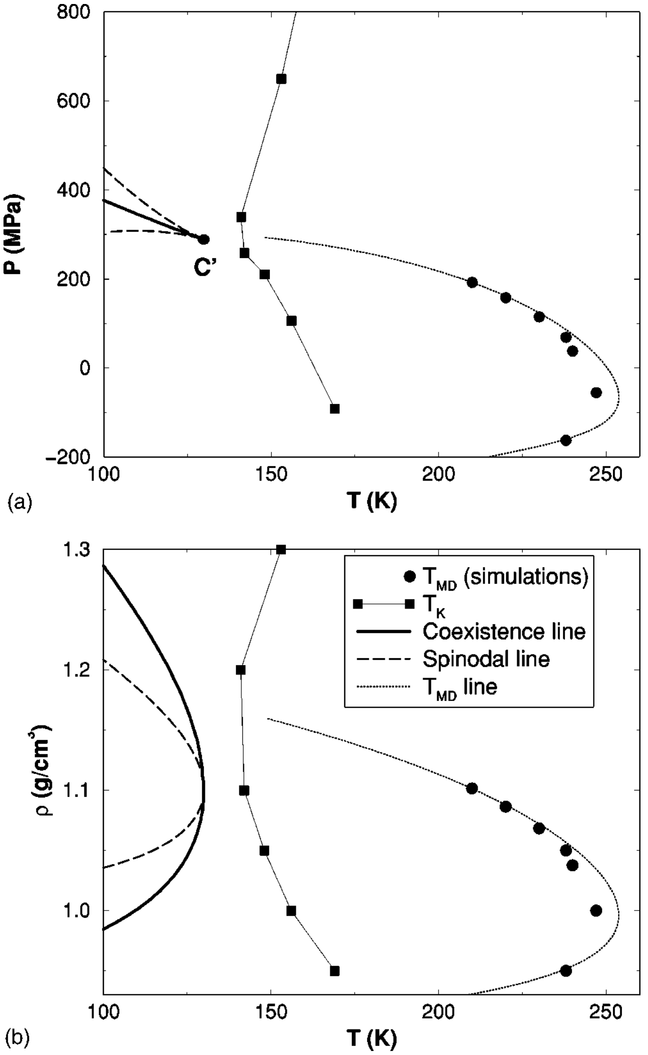

FIG. 6. P-T (upper panel) and ρ-T (lower panel) phase diagrams. Coexistence line, spinodals, and T_{MD} line from our free energy. Circles are T_{MD} points obtained from simulations; squares are the Kauzmann boundary [26] for SPC/E water [21] below which diffusivity is predicted to vanish [27].

IV. CONCLUSIONS

In this paper we have presented a technique of evaluating thermodynamic quantities in the supercooled region, in a T-range where equilibrium simulations are not feasible due to extremely long equilibration times. The relevant result of this analysis, applied to the SPC/E potential, is a clear indication that the free energy surface develops a region of negative curvature on cooling. A liquid-liquid critical point develops, in analogy with the behavior of the ST2 model, for which the location of the critical point is within the region where equilibrated configurations can be calculated.

The predictions reported in this manuscript are based on a functional form for the liquid free energy, supported by recent theoretical predictions [19]. Of course, changes in the temperature dependence related to novel phenomena that may take place outside the range where data are available may break the validity of the extrapolation. In the case of real water, for example, it has been argued that a change in the T dependence of the thermodynamic properties takes place in ‘‘no-man’s land’’ [30]. In the case of SPC/E water, if such change takes place, it must occur at $T\lesssim200$ K, i.e., in the region where simulations are not feasible. This would affect our estimate of the location of the critical point. However, the existence of a region of negative curvature already in the T-region where simulations are feasible supports the possibility that the liquid-liquid critical transition would take place at lower temperatures, independently from the assumed $T^{3/5}$ law.

Our results have a particular relevance, since, as previously noticed, ST2 and SPC/E typically bracket the thermodynamic behavior of the real liquid. The evidence presented here that the SPC/E potential displays a critical point at low T and high P strengthens the possibility that, below the homogeneous nucleation temperature, water may undergo a liquid-liquid (or glass-glass) phase transition; the two distinct liquid phases that would appear below C' could correspond to the two observed amorphous forms of solid water, low density amorphous ice and high density amorphous ice. Indeed, such a transition could be observed in the glassy state even if $T_{C'} < T_K$, as we find for the SPC/E model.

The thermodynamic analysis presented here also allows us to grasp the origin of the presence of the critical point. Indeed, the presence of the critical point arises from the negative concavity of $E(T,V)$, which for $T > T_C$ is compensated by the $-TS(T,V)$ contribution. Note that, as previously observed [10], the negative concavity of $E(T,V)$ already appears in the T region where equilibrium simulations are feasible, suggesting an inevitable phase transition as the product TS becomes progressively smaller with decreasing T. Such negative concavity of $E(V,T)$ is also found in supercooled water [31].

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