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Volume crossover in deeply supercooled water adiabatically freezing under isobaric conditions

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The irreversible return of a supercooled liquid to stable thermodynamic equilibrium often begins as a fast process which adiabatically drives the system to solid-liquid coexistence. Only at a later stage will solidification proceed with the expected exchange of thermal energy with the external bath. In this paper we discuss some aspects of the adiabatic freezing of metastable water at constant pressure. In particular, we investigated the thermal behavior of the isobaric gap between the molar volume of supercooled water and that of the warmer ice-water mixture which eventually forms at equilibrium. The available experimental data at ambient pressure, extrapolated into the metastable region within the scheme provided by the reference IAPWS-95 formulation, show that water ordinarily expands upon (partially) freezing under isenthalpic conditions. However, the same scheme also suggests that, for increasing undercoolings, the volume gap is gradually reduced and eventually vanishes at a temperature close to the currently estimated homogeneous ice nucleation temperature. This behavior is contrasted with that of substances which do not display a volumetric anomaly. The effect of increasing pressures on the alleged volume crossover from an expanded to a contracted ice-water mixture is also discussed. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4803659]

I. INTRODUCTION

With its numerous weird-looking properties water is an anomalous substance par excellence.[1,2] At the same time water probably is the most studied material, in any aspect of its molecular and collective behavior. In this paper we focus on a thermodynamic phenomenon which, over the years, has not so often been under the spotlight of experimental and theoretical investigation, i.e., the adiabatic freezing of metastable supercooled water.[3]

The issue is that of the solidification of a liquid which has been gently cooled below its nominal freezing temperature T_f. Once a crystalline embryo has formed, the solid phase often grows so quickly, in relation to the characteristic heat transfer times, that any significant energy exchange with the external environment is *de facto* precluded. In such conditions freezing occurs as if the liquid were thermally isolated; consequently, the system also heats up while solidifying. Crystallization is typically completed on a much longer time scale, via ordinary heat conduction across the system boundaries.[4] This phenomenon has relevant implications in such diverse areas as atmospheric science[5] and metallurgy.[6]

In this paper we discuss the freezing of supercooled water under adiabatic conditions. The phenomenon is intrinsically irreversible since it entails a transformation from a metastable to a stable condition. Correspondingly, the entropy of the system increases[7] and the final temperature at equilibrium will be higher as well (a phenomenon also known as "recalescence"[6]), since the energy released by the freezing substance cannot be dissipated to the outside environment. Hence, no isothermal transformation of a metastable liquid may occur under adiabatic conditions, independently of which property, be it the volume or the pressure, has been kept fixed. While the energy of the system is conserved at fixed volume, it is the enthalpy that keeps constant at fixed pressure.[6] In general, for not too large undercoolings, the freezing of the metastable liquid is only partial and the nucleated solid coexists with a fraction of the parent liquid at the equilibrium freezing temperature.

As a result of the isenthalpic process illustrated above, a substance may contract or expand. The main goal of this paper is to calculate the molar volume of metastable water at a given subfreezing temperature T and to compare it with the volume of the heterogeneous phase that forms at T_f. The calculation is based on a reference correlation for the bulk thermodynamic properties of water and steam in their respective stable regions of the phase diagram, the so-called IAPWS-95 formulation.[8] We used this scheme to extrapolate the thermodynamic data beyond the currently explored range. Our analysis will show that, also in this respect, water is markedly different from other liquids.

The manuscript is organized as follows. In Sec. II we present our results for liquid water that we compare with those of other liquids in Sec. III. Section IV is finally devoted to some concluding remarks.

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II. VOLUME GAP IN WATER

As anticipated in the Introduction, we suppose that a certain amount of liquid water, initially at the freezing temperature T_f, be slowly undercooled, under isobaric conditions, down to a temperature T. After disconnecting the thermostat, one can observe the spontaneous (or, possibly, externally triggered) nucleation of the solid phase: supercooled water transforms very rapidly, i.e., adiabatically, into a mixture of ice and water coexisting at the freezing/melting point. Similar experiments can actually be performed and their outcome is well known.[9–11] The relative fractions of solid and liquid phases which eventually form at equilibrium depend on the initial undercooling temperature and can be calculated by resorting to the equal-enthalpy condition[6]

$$(1 - x_s)H_l(T_f, P) + x_s H_s(T_f, P) = H_l(T, P)\,, \tag{1}$$

where P is the pressure, H_l and H_s are the enthalpies of the liquid and solid phases, respectively, while $x_s(T, P)$ is the ice mole fraction at equilibrium. We further observe that

$$H_l(T, P) - H_l(T_f, P) = \int_{T_f}^{T} d\tau\, C_P(\tau, P)\,, \tag{2}$$

where C_P is the isobaric heat capacity of the (metastable) liquid, while $L(P) = H_l(T_f, P) - H_s(T_f, P)$ is the latent heat of crystallization (or enthalpy of fusion) released at the equilibrium ice-water phase transition. One thus obtains for the solid mole fraction

$$x_s(T, P) = \frac{1}{L(P)} \int_{T}^{T_f} d\tau\, C_P(\tau, P)\,. \tag{3}$$

The molar volume occupied by the mixture at T_f can then be calculated as

$$V_{\rm mix}(T, P) = [1 - x_s(T, P)]V_l(T_f, P) + x_s(T, P)V_s(T_f, P)\,, \tag{4}$$

where V_l and V_s are the molar volumes of the homogeneous liquid and solid phases, respectively.

We are interested in the dependence of the volumes $V_l(T, P)$ and $V_{\rm mix}(T, P)$ on the undercooling temperature T at a given pressure P. To this end, we resorted to the IAPWS-95 formulation.[8] An assessment on the performance of this scheme when extrapolated into the supercooled-liquid region has been recently carried out by Holten *et al.*[12] These authors found that the IAPWS-95 formulation reproduces the experimental data with fair accuracy at ambient pressure ($P = 0.101325$ MPa), even below the freezing point. However, significant deviations become apparent with increasing pressures. As far as the density is concerned, the overall agreement is relatively good for pressures lower than 80 MPa, but beyond this threshold the temperature slope (i.e., the isobaric thermal expansivity) even has the wrong sign. As for the isobaric specific heat, experimental data are available for supercooled water at atmospheric pressure only. The IAPWS-95 formulation was fitted to the experimental data of Angell *et al.*,[14] who extended their range of measurements down to 236 K. More recently, Archer and Carter[15] also measured the specific heat over the same range; at low temperatures their data show slight systematic deviations from those reported in Ref. 14.

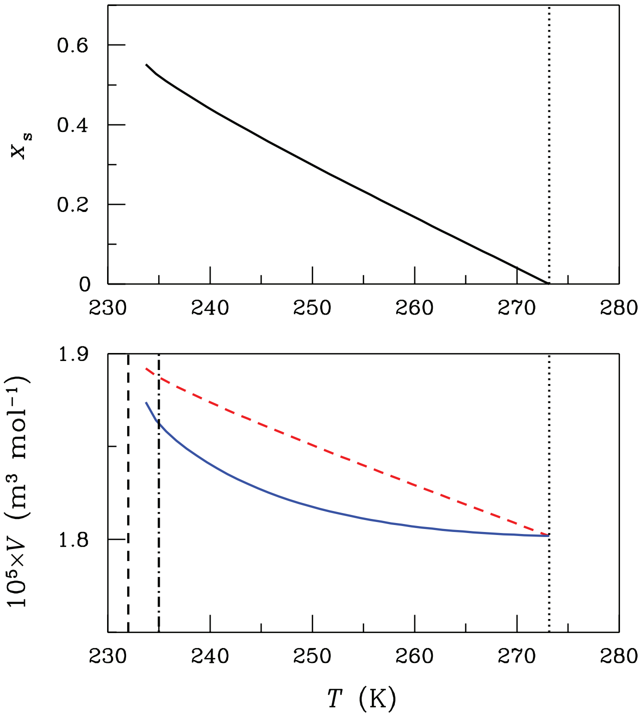

FIG. 1. Water at ambient pressure. Top panel: solid fraction of the ice-water mixture formed at ambient pressure by the metastable liquid, plotted as a function of the undercooling temperature below the freezing point (dotted line); as for the isobaric specific heat of the liquid phase, that is needed to trace the line, we used the data given in Ref. 14, but the result does not change in a discernible way upon using the data of Archer and Carter[15] as an input. Bottom panel: molar volumes of supercooled water (blue continuous line) and of the ice-water mixture (red dashed line) nucleated at ambient pressure, plotted as a function of the undercooling temperature below the freezing point (dotted line); on the lower-temperature side the two curves are terminated at the temperature (~234 K) at which the IAPWS-95 scheme breaks down. The dashed and dotted-dashed lines indicate two different estimates (232 K and 235 K, respectively) of the homogeneous ice nucleation temperature.[16–18]

As for the coexistence properties of hexagonal ice (ice Ih) and liquid water, we used the data tabulated in Ref. 13.

The top panel of Fig. 1 displays the fraction of ice formed at ambient pressure by supercooled water, plotted as a function of the temperature at which the liquid starts nucleating the solid phase. We computed this quantity using both sets of data for the isobaric specific heat that we have just commented on above. Indeed, the two ensuing estimates of x_s can be hardly resolved the one from the other, even at the lowest temperatures. As expected, the lower the undercooling temperature, the larger the energy needed to thermalize the mixture at the freezing temperature and, correspondingly, the larger the fraction of water that solidifies at equilibrium; the value of x_s calculated just before the extrapolation scheme breaks down is close to 60%.

Upon freezing, metastable supercooled water expands, as shown in the bottom panel of Fig. 1 where we compare the volume of liquid water with that of the nucleated ice-water mixture. We see that, with decreasing temperatures, the volume gap between the homogeneous and heterogeneous states grows up to a maximum, attained for $T \approx 245$ K, whence it decreases with a clear indication of an upcoming crossover from an expanding to a contracting regime. On the basis of

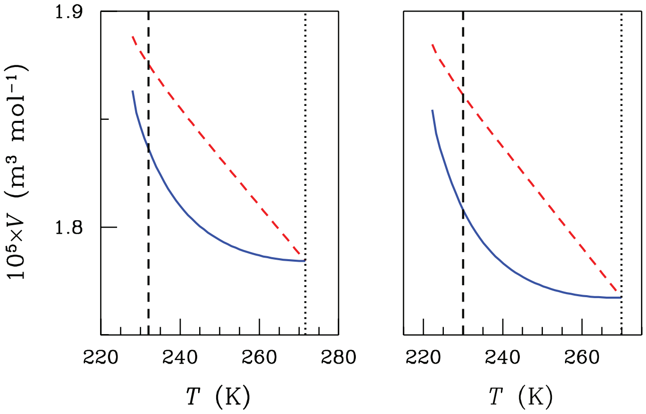

FIG. 2. Molar volumes of supercooled liquid water (blue continuous line) and of the ice-water mixture (red dashed line) nucleated for $P = 20$ MPa (left panel) and $P = 40$ MPa (right panel), plotted as a function of the undercooling temperature below the freezing point (dotted line); on the lower-temperature side the curves are terminated at the temperature at which the IAPWS-95 scheme breaks down. The black dashed line indicates the estimate of the homogeneous ice nucleation temperature reported in Ref. 18.

the present data, we can infer that the crossover might occur for $T_\times \approx 232$ K, i.e., in a range of temperatures where also falls the so-called homogeneous ice nucleation temperature (T_H), i.e., the lowest temperature at which metastable water has been observed so far as a homogeneous liquid.[16–18] We note that for $T = T_\times$ supercooled water would have the same energy, volume, and pressure of the thermodynamically stable ice-water mixture, but a lower entropy and, correspondingly, a lower temperature. It is also interesting to note that the specific volumes of supercooled water, when extrapolated to lower temperatures, and that of ice Ih at the same temperature become apparently equal near T_H. In passing, this latter circumstance and the increasing similarity of the local structures of the two phases in this thermodynamic regime may actually corroborate a "kinetic" interpretation of the stability limit of the homogeneous liquid phase in water.[19]

We extended our analysis at higher pressures with a mandatory *caveat* on the reliability of the extrapolations carried out through the IAPWS-95 formulation in a thermodynamic region where no (even partial) test against experimental data is currently possible for the isobaric specific heat. We restricted our investigation of the volumetric behavior of supercooled water and of the nucleated mixture to a range of pressures lower than 50 MPa since, for larger values of P, the thermal behavior of C_P which the IAPWS-95 formulation predicts along the supercooled-liquid branch displays some likely unphysical features.

Figure 2 shows the temperature-dependence of the molar volumes for two values of the pressure, viz., 20 and 40 MPa. The general trend is similar to that already discussed for water at ambient pressure although the hypothetical volume crossover is apparently shifted below the currently estimated homogeneous nucleation temperatures for such pressures.[18] As for the maximum-volume-gap temperature, it decreases almost linearly with P over this range of pressures as also does the extrapolated crossover temperature $T_\times$. However, it may be hazardous to trust these results other than qualitatively given, on one side, the untested IAPWS-95 behavior of C_P above ambient pressure and, on the other, the presumably provisional current estimates of the homogeneous ice nucleation temperature, as also evidenced by the discrepancies between the values reported in the literature for this quantity at atmospheric pressure.[16–18]

III. COMPARISON WITH OTHER LIQUIDS

In order to assess the extent to which the volumetric behavior of isenthalpically freezing water, as illustrated in Figs. 1 and 2, qualitatively differs from that of a more "standard" liquid, we carried out a similar calculation for *o*-terphenyl (OTP). An interesting aspect of this substance is that, at ambient pressure, its liquid states (both stable and supercooled) as well as its solid states (both crystalline and amorphous) can be observed at close-to-room temperatures. For $P = 0.1$ MPa liquid OTP contracts by about 9% upon freezing at $T_f = 329.35$ K, the released latent heat being 17.191 kJ mol^{-1}.[20] Moreover, the liquid can be easily undercooled down to the glass transition temperature, which falls in the range $243 - 247$ K.[21,22]

Under adiabatic-isobaric conditions supercooled liquid OTP freezes into a heterogeneous solid-liquid mixture in the range of temperatures between T_f and $T_{\text{solid}} = 283.5$ K; correspondingly, the mole fraction of the solid phase linearly increases, with decreasing undercooling temperatures, from 0 (for $T = T_f$) to 1 (for $T = T_{\text{solid}}$): at this latter temperature the liquid transforms entirely into a solid at the freezing temperature. For even larger undercoolings ($T < T_{\text{solid}}$), the temperature of the nucleated (solid) phase is no longer constant but decreases with T from the freezing-point value.

The molar volumes of supercooled liquid OTP and of the phase nucleated at equilibrium are shown in Fig. 3. This picture was produced using the experimental data for the volume and specific heat reported in Ref. 22. In this case, at marked variance with water, (i) the volumes of the supercooled liquid and of the solid-liquid mixture both decrease with decreasing undercooling temperatures; (ii) the volume of the liquid is systematically larger than that of both the solid-liquid mixture and the solid nucleated at equilibrium; (iii) no indication whatsoever of an inversion of this trend emerges from the data at low temperatures.

As far as we can infer, another normal liquid such as carbon tetrachloride also probably behaves as OTP does. No experimental data are apparently available for the molar volume and specific heat of the supercooled liquid phase of CCl_4. However, a polynomial extrapolation of the data from the stable liquid region[23,24] below the freezing temperature ($T_f = 250$ K) suggests that the volumetric aspects associated with the irreversible and isenthalpic freezing of this substance into a solid-liquid mixture are similar to those of OTP.

In order to ascertain whether the behavior of OTP and CCl_4 can be considered to be representative of a larger class of "standard" liquids (i.e., substances which display no water-like volumetric anomaly) one can resort to theoretical models. To this end, we basically need a representation of both the fluid and crystalline phase which incorporates the typical features of the intermolecular potential, i.e., a hard-core

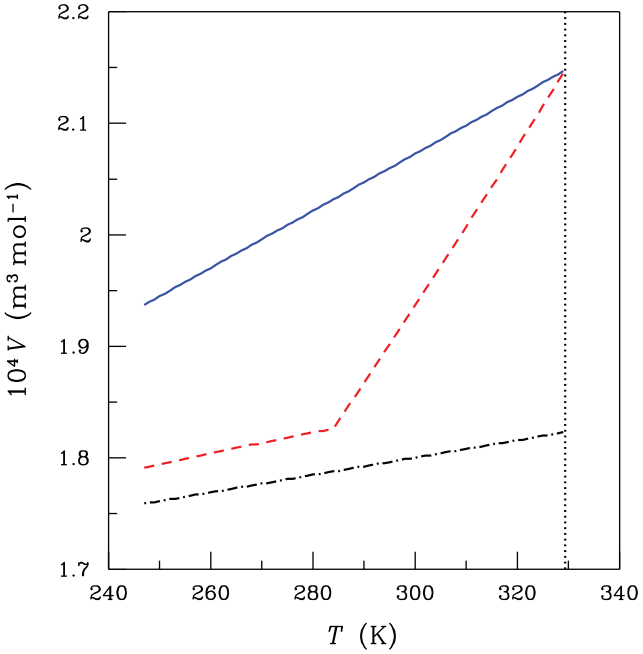

FIG. 3. Molar volumes of o-terphenyl phases at ambient pressure: metastable liquid phase (blue continuous line); stable phase nucleated by the supercooled liquid (red dashed line); stable solid phase (black dashed–dotted line); all curves are plotted as a function of the undercooling temperature in the range bounded by the freezing temperature ($T_{\mathrm{f}} = 329.35$ K) and by an upper estimate of the glass transition temperature ($T_{\mathrm{g}} \approx 247$ K) given in Ref. 22. The cusp singularity exhibited by the red dashed line at the temperature $T_{\mathrm{solid}} = 283.5$ K marks the boundary between two different outcomes of the adiabatic-isobaric freezing undergone by o-terphenyl: for higher temperatures the phase nucleated by the metastable liquid is a solid-liquid mixture at a fixed temperature T_{f}; for lower temperatures ($T < T_{\mathrm{solid}}$), the equilibrium phase is a pure solid ($x_{\mathrm{s}} = 1$) whose temperature decreases with the undercooling temperature, while still keeping higher than that of the parent liquid because of the entropy increase; correspondingly, the nucleated solid has a larger volume than that which the same solid would have at the nucleation temperature of the freezing liquid (data represented by the black dashed-dotted line).

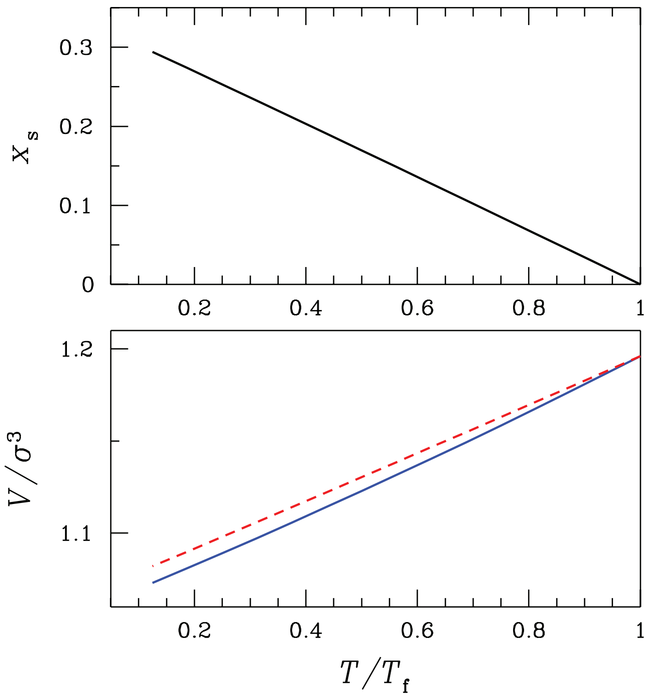

FIG. 4. Adiabatic freezing of a model van der Waals fluid traced along an isobaric path for $P/P_{\mathrm{c}} = 27.68$. Top panel: mole fraction of the solid phase at equilibrium; bottom panel: molar volumes, in units of the hard-core diameter σ, of the metastable liquid (blue continuous line) and of the solid-fluid mixture nucleated at equilibrium (red dashed line). All curves are plotted as a function of the undercooling temperature relative to the value at the freezing point. Adapted from Ref. 27.

repulsion and a short-ranged attraction. In this respect, the combined van der Waals (vdW) theory for the fluid and solid phases developed by Daanoun *et al.*,[25] and further exploited by Coussaert and Baus,[26] does provide a rather flexible, *albeit* approximate and grossly simplified, model which captures the essential features of the problem. Recently, Prestipino has studied the adiabatic freezing of such a model, upon assuming an attractive tail of the form r^{-6}, under a variety of conditions (constant volume, constant pressure, fluid enclosed in a sealed and rigid vessel but in the presence of another gaseous substance).[27] His theoretical strategy was based on the maximum-entropy principle, through which one can recast the determination of the two-phase equilibrium state as a few-parameter optimization problem. The ensuing results for the adiabatic freezing of a supercritical vdW fluid, analyzed along an isobaric path at a pressure $P/P_{\mathrm{c}} = 27.68$, where P_{c} is the critical pressure (the corresponding freezing temperature is 20% lower than the critical temperature), are presented in Fig. 4. As for OTP and carbon tetrachloride, the molar volumes of the metastable vdW liquid and of the solid-liquid mixture nucleated at equilibrium both decrease with decreasing undercooling temperatures. However, in this case the molar volume of the mixture turns out to be systematically larger than that of the parent metastable fluid. Indeed, for substances which contract upon freezing, as is the case of the presently discussed vdW model, whether the heterogeneous phase nucleated at equilibrium shrinks or expands depends on the balance between the reduction in volume experienced by the undercooled fluid with respect to the value at the freezing point and the contraction also undergone by the mixture because of the smaller volume occupied by the nucleated solid (as compared with that occupied, per mole, by the coexisting liquid). For very small undercoolings, such a balance can be quantified upon expanding Eq. (3) to linear terms in $\Delta T = T - T_{\mathrm{f}}$ and then using the outcome for x_{s} in Eq. (4) which then yields

$$V_{\mathrm{mix}}(T, P) = V_{\mathrm{l}}(T_{\mathrm{f}}, P) - \frac{C_P(T_{\mathrm{f}}, P)}{L(P)}\Delta V_{\mathrm{f}}(P)\Delta T, \tag{5}$$

where $\Delta V_{\mathrm{f}}(P) = V_{\mathrm{l}}(T_{\mathrm{f}}, P) - V_{\mathrm{s}}(T_{\mathrm{f}}, P)$ is the volume jump registered at the equilibrium freezing transition; the volume gap $\Delta V(T, P) \equiv V_{\mathrm{mix}}(T_{\mathrm{f}}, P) - V_{\mathrm{l}}(T, P)$ can then be expressed as

$$\Delta V(T, P) = \left[\frac{C_P(T_{\mathrm{f}}, P)}{L(P)}\Delta V_{\mathrm{f}}(P) - \alpha(T_{\mathrm{f}}, P)V_{\mathrm{l}}(T_{\mathrm{f}}, P)\right]\Delta T\,, \tag{6}$$

where $\alpha(T, P)$ is the isobaric thermal expansion coefficient of the liquid phase. It thus follows that the volume gap is positive, as in the present vdW model, if

$$\alpha(T_{\mathrm{f}}, P) > \frac{C_P(T_{\mathrm{f}}, P)}{L(P)}\frac{\Delta V_{\mathrm{f}}(P)}{V_{\mathrm{l}}(T_{\mathrm{f}}, P)}\,. \tag{7}$$

As for water, both $\alpha(T_f, P)$ and $\Delta V_f(P)$ are negative but condition (7) is still verified at ambient pressure. However, with increasing undercoolings the thermal expansivity of metastable liquid water grows (in absolute value) so rapidly that the crossover between the molar volumes of the liquid and of the solid-liquid mixture becomes inevitable unless it is overridden by a loss of thermodynamic stability of the homogeneous liquid phase.

IV. CONCLUSIONS

In this paper we have investigated the volume changes undergone by metastable supercooled water and by a few other liquids when they freeze at constant pressure, either partially or completely, in a spontaneous and irreversible way. We have found that, upon freezing, typical substances which do not display any volumetric anomaly may either contract, as *o*-terphenyl and carbon tetrachloride do, or even expand, as is the case of a theoretical mean-field model based on a combined van der Waals picture of the fluid and solid phases; however, in all such cases, independently of the sign, the volume gap between the molar volume of the supercooled liquid and that of the warmer solid-liquid mixture which eventually forms at equilibrium systematically increases with decreasing undercooling temperatures. In this respect, the behavior of water, as reproduced by the reference IAPWS-95 formulation, is markedly different in that this substance, aside from the opposite temperature trend obviously implied by its volumetric anomaly, expands on freezing; however, the volume gap, after increasing for small undercoolings, is unexpectedly reduced for temperatures lower, at ambient pressure, than ~245 K (a value which moderately decreases with increasing pressures) and manifests a clear tendency to vanish at a temperature close to the (currently estimated) homogeneous ice nucleation temperature. Whether or not a crossover does indeed occur in water from an expanding to a contracting regime, its extrapolated location at the homogeneous ice nucleation threshold is somewhat surprising; however, the present evidence is not sufficient to establish an explicit and coherent connection between the two phenomena, whose implications would certainly require more experimental information in the deep-undercooling region.

Substances as well as theoretical models which also display water-like anomalies will likely share similar features in their volume gap. We refer, for instance, to isotropic one-component systems which undergo, upon isothermal compression, a reentrant melting over some range of temperatures and pressures; such are the systems in which particles softly repel each other through a Gaussian potential,[28–31] a modified inverse-power potential,[32,33] or a Yoshida-Kamakura (YK) potential.[34–36] To confirm this hypothesis, we have carried out some preliminary calculations for the latter potential at reduced pressures $P^\star = 0.3$ and 1 (values in units of the energy and length parameters of the potential) which correspond to two different regions of the phase diagram: in fact, for $P^\star = 0.3$ the YK model behaves "normally," while for $P^\star = 1$ the fluid phase exhibits a water-like volumetric anomaly followed, at lower temperatures, by solidification at a thermodynamic state point located on a reentrant-melting line (see Fig. 2 in Ref. 34). We found that at low pressure the volume gap behaves as in the vdW model described before, while in the anomalous region it looks entirely similar to that of water.

We reserve a concluding remark on a topic that is closely related with the phenomenology of adiabatically freezing metastable liquids: we refer to the famous, and still widely debated, "paradox" that originally attracted the attention of Walter Kauzmann.[37] As is well known, this paradox has to do with the behavior, for increasing undercoolings, of the thermodynamic properties of metastable liquids and, in particular, with the possibility that their entropy may become lower than in the stable crystalline phase at the same temperature. "Certainly it is unthinkable that the entropy of the liquid can ever be very much less than that of the solid," Kauzmann wrote,[37] while, however, conceding that, at small but finite temperatures, such a circumstance could not be excluded *a priori*. This (apparent) paradox has many significant implications, including a potential violation of the third law of thermodynamics as well as the very nature of the glassy state and of the glass transition.[38,39] We just want to emphasize here a specific but enlightening point whose relevance, perhaps, has not been fully appreciated but for one, at least to our knowledge, notable exception:[40,41] as illustrated above in this article, whenever a metastable liquid freezes, it does so irreversibly and adiabatically with an increase of both entropy *and* temperature. Hence, as a matter of principle, it is not appropriate to compare the entropies of the metastable liquid and of the related crystalline phase *at the same temperature*, since no isothermal path does actually connect the two phases. The isothermal freezing of a higher-entropy liquid into a lower-entropy solid is only possible at thermodynamic equilibrium, i.e., as a reversible transformation involving two equally stable phases with different densities. However, the above argument should not preclude one from enquiring into the thermal fate of the entropy of the metastable liquid for increasing undercoolings, at least down to the glass-transition temperature; obviously, such an analysis can be pursued only if an intrinsic stability threshold of the homogeneous liquid phase (vs. crystallization) is not met before, as in water. Indeed, the concrete possibility that the supercooled-liquid condition may actually be monitored down to the Kauzmann temperature, where the configurational entropy of the metastable liquid is deemed to vanish, has been recently investigated[42] and may yield promising insights on the relation between the thermodynamic properties of the crystalline, amorphous, and liquid phases at very low temperatures.

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