Freezing in one-dimensional liquids

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Freezing of liquids in one dimension is studied by a lattice model that is an extension of the model solvent of the hydrophobic attraction. The model in one dimension, which is exactly solvable, exhibits a continuous phase change between a high-temperature disordered "liquid" state and a low-temperature ordered "solid" state but also does exhibit a first-order freezing transition at some finite temperature with either one of the two model parameters taken to be infinite. In this theoretical framework the sharpness of the freezing in one dimension is expressed by a simple function of the microscopic model parameters and thus is related with other macroscopic properties of the substance. These results may account for continuity and discontinuity of the liquid and solid reported for different one-dimensional substances. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1564049]

I. INTRODUCTION

One-dimensional liquids and solids, both crystalline and amorphous, can be found in cylindrical pores with little interconnection (e.g., MCM-41[1]) and in cylindrical tubules with well-defined diameter (e.g., the carbon nanotube[2]), and phase behavior of different substances confined to such pores or tubules is being extensively studied.[3,4] To be sure, such a real system is not in one dimension but in quasi-one-dimension (e.g., the diameter is typically 1.6–10 nm for MCM-41 and 1–3 nm for the single-wall carbon nanotube), but for convenience we refer to such a real system as "one-dimensional" while we make a distinction between one dimension ($d=1$) and quasi-one-dimension ($1<d<2$) when we refer to some theoretical models.

Freezing and melting in equilibrium substances are always first-order transitions and the solid–liquid phase boundary never terminates at a critical point so that there is no continuity of the liquid and solid.[5,6] There is no doubt that this holds for any bulk substances, although no rigorous proof seems to be possible.[6] However, this is not the case for one-dimensional systems ($d=1$) or quasi-one-dimensional systems ($1<d<2$), as the Ising model or the corresponding lattice-gas model does not have a first-order phase transition at all if $d<2$. For real systems such as substances confined to a cylindrical pore, both gradual phase changes, which are similar to the phase transformation above the critical point, and abrupt phase changes, which are similar or virtually identical to the first-order phase transition, are observed in experiments[4,7] and computer simulations.[8–10] We mean by "gradual" that there is a range of temperature (or of some other field variable) over which appreciable changes occur in relevant properties that distinguish one state (e.g., solid) from another (e.g., liquid). The characteristic magnitude of that range, or the sharpness of freezing, would then depend on intermolecular interactions of the system's constituent molecules. It would also depend on the spatial extent of the quasi-one-dimensional system, i.e., the width or diameter of the system, and the material surrounding or in contact with the quasi-one-dimensional system.

We present here a lattice model of gradual freezing in such quasi-one-dimensional substances, which is an extension of the model solvent in a theory of the hydrophobic attraction.[11] In any number of dimension, the model can be mapped to the spin 1/2 Ising model and thus, in one dimension, it is exactly solvable, as the original version. In $d<2$ dimensions with its parameters all finite, it exhibits a gradual phase change between a high-temperature disordered liquid state and a low-temperature ordered solid state; however, if either one of two model parameters is taken to be infinity, it does exhibit a phase transition at a finite temperature. The main goal of this paper is to find in the model framework how the sharpness of freezing is related with the intermolecular interaction and some other macroscopic properties that characterize each substance.

In the following section we define the model, show its correspondence with the Ising model, and obtain explicit formulas for thermodynamic properties of the one-dimensional system. In Sec. III we show the two limiting cases in which the freezing of the one-dimensional liquid takes place as a phase transition and also illustrate qualitatively how the continuous phase behavior changes with changing the model parameters. In Sec. IV we define the sharpness of freezing and obtain an explicit formula for it. Section V provides numerical illustrations in connection with several substances. The results are briefly summarized in Sec. VI. In an Appendix, we relate the model in one dimension with the one-dimensional KH_2PO_4 (KDP) model,[12] which exhibits a phase transition at a finite temperature, showing that in one dimension, the KDP model too is mapped to the Ising model.

II. MODEL

The model is an extension of a lattice model for the hydrophobic interaction,[11] which consists of solvent (water)

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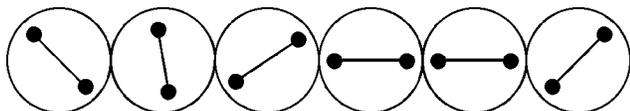
FIG. 1. The model one-dimensional liquid, with each molecule centered at a lattice site and in one of q orientations. The horizontal orientation is identified as the special orientation (state 1).

and solute (hydrophobic) molecules. Now only the solvent part of the original model is considered, and that part is taken to represent any kind of liquid—rather than the particular liquid—with some orientation-dependent intermolecular interaction.

A schematic picture of the model is shown in Fig. 1. Each molecule occupies one lattice site and may be in any one of q states or orientations. There is one special orientation identified as state 1. Only neighboring molecules interact with each other and the interaction energy depends on their orientations: Two neighboring molecules both in the special orientation (state 1) interact with each other with interaction energy w; neighboring molecules only one of which is in the special orientation interact with each other with energy $\epsilon > w$; and neighboring molecules of which neither is in the special orientation interact with each other with energy $u > w$. The parameters of this model are then $q - 1 > 0$, $u - w > 0$, and ϵ. The lowest pair interaction energy w may be due to a directional bonding (e.g., the hydrogen bond in ice or the covalent bond in crystal silicon) or any other mechanism. The higher energy u represents the pair interaction energy that the majority of two neighboring molecules would have at high temperatures. The energy ϵ for two neighboring molecules in the special and nonspecial orientations might be greater or less than u, and the sign and magnitude of $\epsilon - u$ appropriate for a given substance are dependent on the anisotropic intermolecular interaction, for example, due to the shape of a nonspherical repulsive core of the molecule, the secondary directional bonding, and so on.

We consider that the system with almost all the molecules in the special orientation corresponds to a solid state whereas the one with almost all the molecules in any other orientations corresponds to a liquid state. The two conditions $u - w > 0$ and $\epsilon - w > 0$ are necessary for the lowest-energy state to be the perfect solid state, in which every molecule is in the special orientation.

The difference between the original model[11] and the present model is that the former assumes $\epsilon = u$ whereas the latter does not. With this generalization the model may be taken to represent a wider range of different intermolecular interactions, and so different substances, than the original model represents. Yet the extended model is still exactly solvable in one dimension as shown below. [The assumption $\epsilon = u$ in the original model was perfectly reasonable because then the model represented water exclusively, and the distinction other than the two states, hydrogen-bonding (w) and nonbonding (u), was unimportant.]

Let N_1, N_0, and N be the number of molecules in the special orientation, the number of molecules in any other orientation, and the total number of molecules, respectively. Also let N_{11}, N_{01}, and N_{00} be the number of pairs of neigh-

boring molecules both in the special orientation, the number of neighboring pairs only one of which is in the special orientation, and the number of neighboring pairs both in any other orientations, respectively. Then the partition function Z is

$$Z = \sum e^{-(wN_{11} + \epsilon N_{01} + uN_{00})/kT}$$

$$= \sum_{0,1} (q-1)^{N_0} e^{-(wN_{11} + \epsilon N_{01} + uN_{00})/kT}, \quad (1)$$

where the first sum Σ runs over all the q orientations for each molecule whereas the second sum $\Sigma_{0,1}$ runs over state 1 (the special orientation) and state 0 (any one of other $q-1$ orientations) for each molecule; an additional factor $(q-1)^{N_0}$ in the second sum is due to the degeneracy $q-1$ for each molecule in state 0. The summand in (1) may be expressed in terms of N_1 and N_{01} (because of the identities $N_0 = N - N_1$, $N_{00} = (CN_0 - N_{01})/2$, and $N_{11} = (CN_1 - N_{01})/2$ with C the coordination number), and then the partition function is

$$Z = \sum_{0,1} e^{-E/kT}, \quad (2)$$

with

$$E = \left[-\frac{C}{2}(u-w) + kTQ \right] N_1 + \frac{P}{2}(u-w)N_{01}$$

$$+ \left[\frac{C}{2}u - kTQ \right] N, \quad (3)$$

where

$$P = 1 + 2\left(\frac{\epsilon - u}{u - w} \right), \quad Q = \ln(q - 1). \quad (4)$$

Thus this extended model is equivalent to an Ising spin model or to the corresponding one-component lattice gas as the original model is.[13] With a choice that state 1 (the special orientation) corresponds to spin ↑ (the direction of the field) in the Ising model, the external magnetic field H and the spin–spin interaction energy J in the Ising model are related to $u - w$, Q, and P by

$$H = \frac{C}{4}(u-w) - \frac{1}{2}kTQ, \quad J = \frac{P}{4}(u-w). \quad (5)$$

For the one-component lattice gas with the interaction energy $-\varepsilon$ and the dimensionless activity ζ, the correspondence is

$$\varepsilon = P(u-w), \quad \zeta = e^{-C(\epsilon - u)/kT}/(q-1). \quad (6)$$

In one dimension, the exact calculation of the partition function Z is done by the standard transfer matrix method.[14] The transfer matrix is now

$$\mathbf{V} = \begin{pmatrix} a & b \\ b & c \end{pmatrix},$$

with

$$a = e^{-w/kT}, \quad b = e^{-\epsilon/kT + Q/2}, \quad c = e^{-u/kT + Q}, \quad (7)$$

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and so if λ_1 and λ_2 are the eigenvalues of $\mathbf{V}$ the partition function is $Z=\lambda_1^N+\lambda_2^N$. In the thermodynamic limit $N\to\infty$, only the larger eigenvalue, λ_1, is significant so that

$$Z^{1/N}=\lambda_1=\frac{c}{2}[x+1+\sqrt{X}], \tag{8}$$

where

$$x=\frac{a}{c}=e^{(u-w)/kT-Q}, \quad y^2=\frac{b^2}{ac}=e^{-P(u-w)/kT},$$

$$X=(x-1)^2+4xy^2. \tag{9}$$

If we now introduce a reduced temperature

$$T^*=\frac{QkT}{u-w}, \tag{10}$$

then x and y^2 are expressed as

$$x=\exp\left[Q\left(\frac{1}{T^*}-1\right)\right], \quad y^2=\exp[-PQ/T^*]. \tag{11}$$

Thermodynamic properties are then calculated by differentiations of the partition function or the free energy $f=-kT\ln\lambda_1$ per molecule. For the internal energy $\phi=U/N$ per molecule,

$$\phi=\frac{\partial(f/T)}{\partial(1/T)}=u-\frac{(u-w)x}{x+1+\sqrt{X}}\left[1+\frac{x-1-2(P-1)y^2}{\sqrt{X}}\right], \tag{12}$$

or in a reduced form

$$\phi^*=\frac{\phi-w}{u-w}=1-\frac{x}{x+1+\sqrt{X}}\left[1+\frac{x-1-2(P-1)y^2}{\sqrt{X}}\right]. \tag{13}$$

For the entropy s per molecule

$$s/k=\frac{\phi-f}{kT}=\frac{Q\phi^*}{T^*}+\ln\left[\frac{x+1+\sqrt{X}}{2x}\right]. \tag{14}$$

We can also calculate the heat capacity per molecule, which is, in a reduced form

$$c^*=\frac{\partial\phi^*}{\partial T^*}=\frac{Q}{T^{*2}}\left\{\phi^*(1-\phi^*)\right.$$

$$\left.+\frac{2xy^2P(P+1)\left[x^2+2\left(1-\frac{1}{P}\right)(y^2-1)x+\frac{P-1}{P+1}\right]}{(x+1+\sqrt{X})X^{3/2}}\right\}. \tag{15}$$

The average mole fraction $\rho_1=\langle N_1/N\rangle$ of molecules in the special orientation is given by

$$\rho_1=1-\frac{\partial\ln\lambda_1}{\partial Q}$$

$$=1-\frac{1}{x+1+\sqrt{X}}\left[1+\sqrt{X}-\frac{x(x-1+2y^2)}{\sqrt{X}}\right]. \tag{16}$$

This may be taken as the order parameter of the phase change, and will be used later in defining the sharpness of gradual freezing.

When the parameters are all finite and satisfy the restrictions ($q-1>0$, $u-w>0$, and $\epsilon>w$), the phase behavior in the low- and high-temperature limits is immediately obtained from these equations. In the limit $T^*\to0$, we have $x\to\infty$, $\sqrt{X}\simeq x$, and $y^2/x=0$; then from (12) we find for the energy per molecule that $\phi=w$. In the same limit, from (14) and (16), we find $s/k=0$ and $\rho_1=1$. (If $\epsilon<w$ provided the other two conditions are still satisfied, we would find $\phi=\epsilon$ and $\rho_1=\frac{1}{2}$ in the low-temperature limit, which is not the state we defined as "solid.") On the other hand, in the high-temperature limit $T^*\to\infty$, where $x=1/(q-1)$, $y^2=1$, and $\sqrt{X}\simeq x+1$, we find that $\phi\simeq[(q-1)/q]^2u+(1/q^2)w+[2(q-1)/q^2]\epsilon$, $s/k\simeq\ln q$, and $\rho_1\simeq1/q$. These are indeed what we can anticipate simply from a fact that occurrence of any one of the q orientations is equally likely at high T.

III. CONTINUITY AND DISCONTINUITY

The microscopic parameters $u-w$ and $Q=\ln(q-1)$ in this model have direct connections with experimentally measurable macroscopic properties of the system: The energy (or enthalpy) and entropy changes on melting. This is seen most clearly in the limit $\epsilon\to\infty$, or equivalently $P\to\infty$, which corresponds to a constraint that any two neighboring molecules must be either both in the special orientation or both not in the special orientation. In this limit, $y^2=0$ and $X=(x-1)^2$ so that from Eq. (12)

$$\phi=u-\frac{(u-w)x}{x+1+\sqrt{(x-1)^2}}\left[1+\frac{x-1}{\sqrt{(x-1)^2}}\right]. \tag{17}$$

Since $x-1$ changes its sign at $T=(u-w)/kQ$ or $T^*=1$, there is a discontinuity in energy ϕ as a function of temperature

$$\phi=\begin{cases} w & (T^*<1) \\ u & (T^*>1) \end{cases}. \tag{18}$$

That $\phi=w$ when $T<(u-w)/kQ$ indicates that below that temperature the system is in the perfect solid state in which every molecule in the system is in the special orientation or $\rho_1=1$, as is verified from Eq. (16). Thus we may identify

$$T_f=(u-w)/kQ, \tag{19}$$

with the freezing point, and $u-w$ and kQ with the latent heat and the entropy change per molecule upon the melting transition, respectively. From Eq. (14) again with $y=0$ and $X=(x-1)^2$, we find the corresponding discontinuity in the entropy: $s/k=0(T^*<1)$ and $s/k=Q(T^*>1)$, as we expected.

The limit $P\to\infty$ corresponds to the coupling constant $J\to\infty$ or the reduced temperature $kT/J\to0$ in the Ising model [see (5)]. Thus, the phase transition observed at the finite temperature T_f in this one-dimensional model with P infinite is mapped to the phase transition as in the one-dimensional Ising model at $H=0$ and $kT/J=0$. In the Appendix, we will see that the same kind of mapping holds for the phase transition in the one-dimensional KDP model.[12]

As soon as we eliminate the constraint on the mutual orientations of any two neighboring molecules (i.e., if ϵ is taken to be finite), the one-dimensional system no longer undergoes a phase transition, and so we lose the exact correspondences of $u-w$, kQ, and T_f with the latent heat, the entropy change, and the freezing point; but we would still find analogous correspondences: $u-w$ with the difference in energy between a high-temperature phase (liquid) and a low-temperature phase (solid), kQ with the corresponding difference in entropy, and T_f with the temperature at which the order parameter $\rho_1 = 1/2$, i.e., the midpoint between $\rho_1 = 0$ (liquid) and 1 (solid). Here and below, we shall call T_f in (19) the temperature of phase change if the phase change is continuous. Notice that $T = T_f$ or $T^* = 1$ corresponds to $H = 0$ in the underlying one-dimensional Ising model, as is seen from Eq. (5) with $C = 2$, whereupon the numbers of $\uparrow$ and $\downarrow$ spins are equal.

The following numerical illustration shows qualitatively that not only ϵ (or P) but also $q-1$ (or Q) affect the continuity of liquid and solid states in one dimension. An exact account of how P and Q change the sharpness of freezing will be given in Sec. IV.

To start the numerical illustration with some physically reasonable choice of parameter values, we first note that $P = 1$ corresponds to the condition originally assumed in the model solvent (water).[11] Second, the original model in one dimension with $Q = 2.8$ (and with some particular values of the other parameters) reproduces best the solubility of methane in *bulk* water over the temperature interval 273–328 K.[15] If the parameter value $Q = 2.8$ is chosen, the present model would have 23 J mol^{-1} K^{-1} as the entropy difference between liquid and solid states, which is very close to the entropy change in *bulk* water, 22 J mol^{-1} K^{-1}, at the melting point. In the following illustration, we use $P = 1$ and $Q = 2.8$ as standard values, though now the one-dimensional model represents not bulk but one-dimensional (or quasi-one-dimensional) systems.

Figure 2 shows ϕ^* and c^* as functions of T^* for each of $P = 1$, 2, and 8 with $Q = 2.8$. It is clear from Fig. 2(a) that the larger the parameter P (with fixed Q) the sharper the slope of ϕ^* at $T^* = 1$. Equivalently, Fig. 2(b) shows that the maximum of the specific heat increases and the position of the maximum approaches $T^* = 1$ with increasing P. When $P = 8$ and $Q = 2.8$, these functions $\phi^*(T^*)$ and $c^*(T^*)$ are indistinguishable from a step function and a delta function ($c_{max}^* = 5.1 \times 10^4$), respectively, and so the phase change is then virtually a first-order phase transition. This is consistent with what we already saw in the asymptotic form (18) as $P \to \infty$.

Figure 3 shows ϕ^* and c^* as functions of T^* with the different values of $Q = 2.8$, 5, and 12 and with a common value of $P = 1$. It is now apparent that the larger the parameter Q (with fixed P) the sharper the slope of ϕ^* at $T^* = 1$ and, equivalently, the higher the maxima of c^*. When $Q = 12$ with $P = 1$, $\phi^*(T^*)$ and $c^*(T^*)$ become practically a step function and a delta function ($c_{max}^* = 1.2 \times 10^3$), respectively, just as they do when P is large while Q is not.

The limit $Q \to \infty$ (at fixed P and T^*) means, from Eq. (11), that (a) $y^2 \to 0$ *and* (b) $x \to \infty$ (if $T^* < 1$) or 0 (if T^*
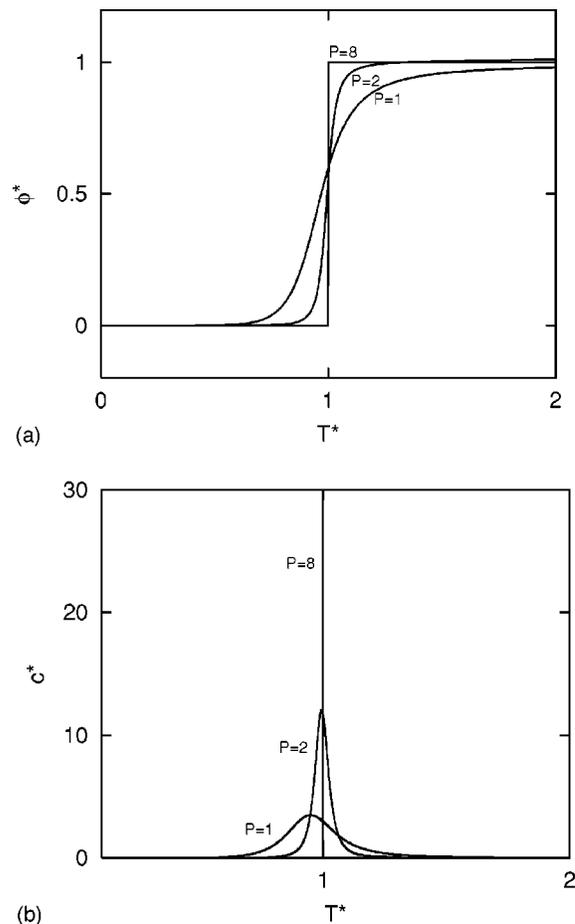
FIG. 2. (a) ϕ^* and (b) c^* as functions of T^*, with the parameter values $P = 1$, 2, and 10 and $Q = 2.8$.

> 1). The first limit (a) leads to (18), as we already saw, while the second limit (b), too, gives rise to the same discontinuity or infinite sharpness of the phase change (even if y^2 were fixed finite). Thus we now know that in the limit $Q \to \infty$ with fixed P the system undergoes a phase transition at $T^* = 1$ as in the limit $P \to \infty$ with fixed Q. This verifies the numerical results for $\phi^*(T^*)$ and $c^*(T^*)$ with large Q. We also notice that the effect of increasing Q on the sharpness of the phase change would be stronger than that of increasing P. For increasing Q means both (a) and (b) whereas increasing P leads to (a) alone. We will see this in explicit expressions of the sharpness given in the following section; here we just note that the two limits $P \to \infty$ and $Q \to \infty$ have different physical meanings, i.e., the former imposes an infinitely strong constraint on the mutual orientation of neighboring molecules whereas the latter makes the ratio $1/(q-1)$ of the numbers of special to nonspecial orientations infinitely small.

IV. SHARPNESS OF FREEZING

In principle, the sharpness of the phase change can be measured from the temperature-dependence of any property relevant to the phase change such as the energy, the entropy, the heat capacity, etc. We use the order parameter ρ_1 and measure the sharpness by a characteristic range of tempera-

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(a)

(b)
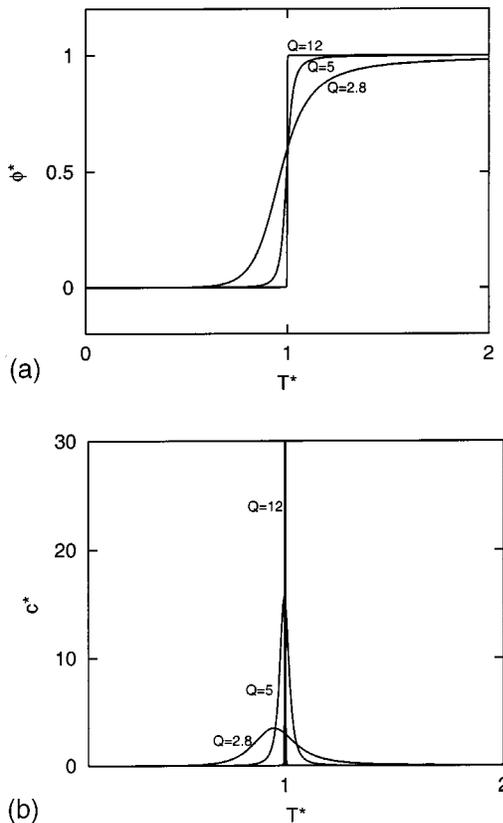
FIG. 3. (a) ϕ^* and (b) c^* as functions of T^*, with the parameter values $Q = 2.8$, 5 and 12 and $P = 1$.

FIG. 4. Sketch of ρ_1 as a function of T^* (when $P = 1$ and $Q = 1$) and the sharpness of the phase change $\Delta T^* = T_0^* - T_1^*$. On the line tangent to $\rho_1(T^*)$ at $T^* = 1$, one has $\rho_1 = 1$ at T_1^* and $\rho_1 = 0$ at T_0^*.

ture in which the system undergoes much of the phase change between liquidlike and solidlike states and outside of which the system's state remains either liquidlike or solidlike. With $\rho_1(T^*)$, such a quantitative measure ΔT^* is defined as

$$\Delta T^* = -\left(\frac{d\rho_1}{dT^*}\right)^{-1}_{T^*=1} = -\left(\frac{dT^*}{d\rho_1}\right)_{\rho_1 = 1/2}. \tag{20}$$

The derivative of ρ_1 is evaluated at $T^* = 1$, where $\rho_1 = 1/2$, because it is the temperature around which the significant phase change occurs and at which the first-order transition would occur if $P \rightarrow \infty$ or $Q \rightarrow \infty$. As shown in Fig. 4, ΔT^* is a "distance" between the two temperatures T_1^* and T_0^* at each of which ρ_1 would be 1 (all molecules in the special orientation) and 0 (none in the special orientation), respectively, if ρ_1 were a linear function of T^* tangential to the actual $\rho_1(T^*)$ at $T^* = 1$.

From Eq. (16) we obtain an involved expression of $d\rho_1/dT^*$ as a functions of T^*, but if we evaluate this at $T^* = 1$, where $x = 1$ and $y^2 = \exp(-PQ)$, we find for ΔT^* a simple analytical expression

$$\Delta T^* = \frac{4}{Q}\exp(-PQ/2). \tag{21}$$

This is a main result for the sharpness of the freezing. We find from this that $\ln \Delta T^*$ decreases linearly with increasing P for given Q and decreases more strongly, due to an extra term $-\ln Q$, with increasing Q for given P. This verifies the

qualitative trends seen in the numerical results in Sec. III and also confirms the earlier anticipation that the effect of increasing Q is stronger than that of increasing P. For large P and Q

$$\ln \Delta T^* \sim -PQ/2, \tag{22}$$

so that the effects of P and Q on ΔT^* would be equivalent.

The range of the reduced temperature ΔT^* over which much of the phase change occurs may also be identified with $\Delta T/T_f$, the ratio of the range of temperature ΔT to the temperature T_f of phase change. In the actual temperature scale, we find from (21) with (10)

$$\Delta T = \frac{4T_f}{Q}\exp(-PQ/2) = \frac{4(u-w)}{kQ^2}\exp(-PQ/2). \tag{23}$$

This means that the Q dependence of ΔT (with other parameters fixed) is even stronger than that of ΔT^*.

Instead of $-d\rho_1/dT^*$ in (20), we could have chosen $c^* = d\phi^*/dT^*$ at $T^* = 1$ as a measure of the sharpness of the phase change. From (15) with $T^* = 1$, we find

$$c^*(T^* = 1) = \frac{Q}{4}e^{PQ/2}\left[1 + \left(\frac{P}{1 + e^{PQ/2}}\right)^2\right], \tag{24}$$

which shows how the (reduced) heat capacity at the temperature of the phase change increases with increasing P or Q. When the product PQ is large, the second term in the square brackets in (24) is negligible, and so we then find

$$1/c^*(T^* = 1) \simeq \frac{4}{Q}e^{-PQ/2}. \tag{25}$$

This is identical with ΔT^* in (21), the sharpness of the freezing defined in terms of the order parameter ρ_1. Thus, choosing c^*, instead of $d\rho_1/dT^*$, at $T^* = 1$ to define the sharpness of the phase change will not affect our conclusions. We could have also chosen c^* at its maximum, instead of at $T^* = 1$; it just results in a complicated expression, and does not change our conclusions because the temperature at which

c^* is maximum is always close to, and with P or Q large is essentially equal to, the temperature of phase change $T^* = 1$.

V. NUMERICAL ILLUSTRATION

Now that the sharpness of freezing ΔT^* is related to the material-dependent model parameters via the simple analytical form (21), we estimate the magnitudes of ΔT^* for several different sets of the parameter values, each set being in connection with a real substance. Our purpose here is neither to fit experimental results on ΔT^* for (quasi) one-dimensional liquids, which are scarcely available, nor to make accurate prediction of ΔT^* for such substances but to know how large or small ΔT^* might be if the model parameters have some values in some connection with real substances. Thus, we make such choice of parameter values with the simplest possible assumptions. First, for simplicity, we assume that $P = 1$, or equivalently $\epsilon = u$. This means that any material-dependence in P is ignored and that the model is now formally identical to the original model. [In general P might be greater or less than 1 (i.e., $\epsilon > u$ or $\epsilon < u$) depending on a material; but there is no obvious correspondence between P and some macroscopic properties of the material and, though its microscopic significance is clear, there are not enough experimental results as yet for the required microscopic information.] Second, we assume $Q = \Delta S/k$ for each substance, i.e., that the entropy difference kQ between typical liquid and solid states for a one-dimensional substance is equal to the measured entropy change ΔS in the melting transition of the bulk substance. Finally, we assume $u - w = \Delta H$ for each substance, where ΔH is the measured latent heat of the bulk substance. Then $T_f = (u - w)/kQ = \Delta H/\Delta S = T_f^b$, where T_f^b is the melting point of a bulk substance, and so the sharpness of the freezing $\Delta T (= T_f \Delta T^*)$ in units of degree K is also determined for each case.

With these assumptions, we evaluate ΔT^* and ΔT for water, ethanol, hydrogen sulfide, and silicon. For water ($\Delta S = 22$ J mol^{-1} K^{-1}, $T_f^b = 273$ K), we find $\Delta T^* = 0.4$ and $\Delta T = 110$ K. This magnitude of ΔT means that the phase change is nothing but the continuous one. For this model with the above assumptions, this also means that liquid "water" in one dimension does not freeze at temperatures as low as 273 K$-\Delta T/2 \approx 220$ K. For ethanol ($\Delta S = 31.6$ J mol^{-1} K^{-1}, $T_f^b = 159$ K), the corresponding results are $\Delta T^* = 0.16$ and $\Delta T = 25$ K; the phase change is much sharper in either ΔT^* or ΔT, than for water; but there would be still no doubt about the continuity of liquid and solid states. For hydrogen sulfide ($\Delta S = 45.8$ J mol^{-1} K^{-1}, $T_f^b = 187.6$ K), although the entropy of melting is only twice as great as that of water, we find $\Delta T^* = 1.3 \times 10^{-4}$ and $\Delta T = 0.02$ K, an extremely narrow temperature range compared to the previous two examples. When as in this case the magnitude of ΔT is as small as the typical precision in melting point measurements, the freezing is likely to be identified as a first-order phase transition. Finally, consider silicon ($\Delta S = 297.6$ J mol^{-1} K^{-1}, $T_f^b = 1687$ K) as an extreme case. We then find $\Delta T^* = 1.9 \times 10^{-9}$ and $\Delta T = 3.2 \times 10^{-6}$ K. With

this infinitesimal magnitude of ΔT, the freezing of the one-dimensional substance is practically a first-order phase transition.

The sharpness of freezing is also strongly dependent on P (see Fig. 2), and indeed ΔT^* vanishes exponentially rapidly with P as in (21). Had $P = 0$ [i.e., $\epsilon - u = -\frac{1}{2}(u - w) < 0$] been chosen in the above numerical illustration, ΔT for "hydrogen sulfide" would have been 49 K instead of 0.02 K, and for the other three cases would have been greater than 49 K. On the other hand, with $P = 2$ [i.e., $\epsilon - u = \frac{1}{2}(u - w) > 0$], ΔT would be 29 K for "water," 3.8 K for "ethanol," 1×10^{-5} K for "hydrogen sulfide," and 5×10^{-14} K for "silicon."

These results mean that freezing or melting of a real (quasi) one-dimensional substance may be either so gradual that one can see clearly the continuity of liquid and solid or so sharp that one cannot distinguish it from the first-order transition, depending strongly on what the substance is. The sharpness of the phase change ΔT of each substance may indeed be inferred from the enthalpy change (latent heat) and the entropy change in the melting transition of the bulk substance. However, if we really wish to evaluate ΔT for a given substance, we need some additional experimental or theoretical data that can be used to determine the parameter P for the substance.

VI. SUMMARY

The sharpness of the freezing in one-dimensional liquids is related with the two microscopic model parameters P and Q associated with, respectively, the energetic and entropic feature of the intermolecular interaction. In either limit $P \to \infty$ or $Q \to \infty$ the model exhibits the first-order phase transition at a finite temperature $T_f = (u - w)/kQ$ with the energy change $u - w$ and the entropy change kQ. With the product PQ finite, the sharpness of the phase change ΔT^* (i.e., melting or freezing) was expressed by the simple analytical function (21) of P and Q.

In numerical illustration, ΔT^* and ΔT (in units of K) were evaluated for several different sets of the parameter values, each set being related to each of water, ethanol, hydrogen sulfide, and silicon. Within the range of these parameters the freezing behavior in one dimension is found to vary from an extremely gradual phase change (in the case of water) to virtually a first-order phase change (in the case of silicon). This suggests that freezing of a (quasi) one-dimensional liquid may be observed to be either continuous or discontinuous, strongly depending on the material. It is remarked that the sharpness of the phase change of a substance in (quasi) one dimension may be inferred from the latent heat and the entropy change in the melting transition of the bulk substance.

The model is mapped to the Ising model in any dimension. In the Appendix, the extended one-dimensional KDP model (one-dimensional Takagi model) is also mapped to the one-dimensional Ising model, and then the correspondence between the present model with P infinite and the one-dimensional KDP model is established.

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ACKNOWLEDGMENTS

APPENDIX: ONE-DIMENSIONAL KDP MODEL

We show a definite relation between the present model in one dimension and the one-dimensional KDP model.[12] The latter model, a one-dimensional analog of the Slater KDP model,[16] was proposed by Nagle as a simplest example that presents a phase transition at some finite temperature, and indeed is an illuminating model as taken as an exercise in a standard textbook.[17] We first briefly define the one-dimensional KDP model and then relate this model to the one-dimensional Ising model.

The one-dimensional KDP model consists of a one-dimensional array of phosphate (PO_4^{3-}) groups that has a pair of protons H^+ (and a single potassium ion K^+ playing no role in the model) between any two neighboring phosphate groups. It is assumed that each pair of the protons takes one of four possible configurations, which we here represent by $\leftarrow$, $\rightarrow$, $\uparrow$ and $\downarrow$, and that the total energy of the system is the sum of the pair interaction energies between two neighboring "arrows:" 0 if they are $\leftarrow\leftarrow$ or $\rightarrow\rightarrow$; $u > 0$ if they are $\uparrow\uparrow$, $\uparrow\downarrow$, $\downarrow\uparrow$, or $\downarrow\downarrow$; and $+\infty$ otherwise. (Our language defining the energy is different from the original one in which the total energy is the sum of phosphate group energies; but they are equivalent.) The partition function of the system of N molecules with the periodic boundary condition is $Z_N = 2 + 2^N \exp(-Nu/kT)$ because there are two ground states with energy 0 and 2^N excited states with energy Nu, and thus the internal energy per molecule is discontinuous at $T = u/(k \ln 2)$ in the thermodynamic limit.

To find a connection with the Ising model, first assign a finite energy $\epsilon > 0$ for two neighboring arrows one of which is either $\leftarrow$ or $\rightarrow$ and the other is either $\uparrow$ or $\downarrow$. This modified model is the one-dimensional analog of the Takagi model.[18] Second, classify arrows into two types: type 1 if $\leftarrow$ or $\rightarrow$ and type 0 if $\uparrow$ or $\downarrow$, and then let N_1 and N_0 be the numbers of arrows of each type, respectively, and let N_{00}, N_{11}, and N_{01} be the numbers of two neighboring arrows both being type 0, both being type 1, and one being type 0 and the other being type 1, respectively. Then the partition function Z_{KDP} is expressed as

$$Z_{KDP} = \sum_{0,1} 2^{N_0} 2^{N_{01}/2} e^{-(\epsilon N_{01} + u N_{00})/kT}, \tag{A1}$$

where the sum $\Sigma_{0,1}$ runs over the two types for each arrow. The factor 2^{N_0} is the degeneracy for the N_0 arrows of type 0 whereas the other factor $2^{N_{01}/2}$ is the degeneracy for the $N_{01}/2$ *domains* of type 1 arrows, for there are only two possible states for each domain ("$\leftarrow\leftarrow\cdots\leftarrow$" or "$\rightarrow\rightarrow\cdots\rightarrow$") and there are $N_{01}/2$ such domains. If we rewrite (A1) using the identities among $N, N_0, N_1, N_{00}, N_{11}$, and N_{01} [those above Eq. (2)] with $C = 2$,

$$Z_{KDP} = \sum_{0,1} e^{-E/kT}, \tag{A2}$$

with

$$E = [-u + kT \ln 2]N_1 + [\epsilon - \tfrac{1}{2} - \tfrac{1}{2}kT \ln 2]N_{01}$$
$$+ [u - kT \ln 2]N. \tag{A3}$$

Thus the one-dimensional Takagi model can be mapped onto the Ising model via the relations

$$H = \tfrac{1}{2}u - \tfrac{1}{2}kT \ln 2, \quad J = \tfrac{1}{2}\epsilon - \tfrac{1}{4}u - \tfrac{1}{4}kT \ln 2. \tag{A4}$$

From the second relation, we find that the one-dimensional KDP model, which is restored in the limit $\epsilon \to +\infty$, corresponds to the Ising model with the coupling constant J infinity or the reduced temperature kT/J zero; thus, the phase transition at $T = u/(k \ln 2)$ in the one-dimensional KDP model is mapped to the discontinuity in the magnetization at $H = 0$ in the one-dimensional Ising model at $kT/J = 0$. In Sec. III, we saw exactly the same mapping as this for the phase transition in the model of freezing in one dimension with the parameter P infinite. Thus, the present model with P infinite has a close connection with the KDP model when both are in one dimension.

The close connection between the two models will be explicit if the energy of the ground state is taken to be 0 in the model of freezing, i.e., $w = 0$. It then follows from Eq. (5) with $C = 2$ and $Q = \ln(q-1)$ that

$$H = \tfrac{1}{2}u - \tfrac{1}{2}kT \ln(q-1), \quad J = \tfrac{1}{2}\epsilon - \tfrac{1}{4}u. \tag{A5}$$

Comparing these with the relations (A4), we find that the one-dimensional Takagi model is identical with the model of freezing in one dimension with $q = 3$, except the last term, $-\tfrac{1}{2}kT \ln 2$, in the second equation in (A4), which is due to the twofold degeneracy for each low-energy domain of type 1 arrows in the former model. This difference will be irrelevant if $\epsilon \to \infty$. Then, when both are in one dimension, the KDP model (the Takagi model in the limit $\epsilon \to \infty$) is exactly the same as the model of freezing with $q = 3$ and P infinity.

A unique feature of the present model is that there is another route to the phase transition in one dimension; the limit $Q \to \infty$. The parameter Q or q is the entropic one rather than the energetic one (P or ϵ), and the limit $Q \to \infty$ corresponds not to $J \to \infty$ but to an infinitely large change in H for a given finite temperature change in the Ising model [see the first relation in (5)].

The two different ways of enabling the one-dimensional model to exhibit the phase transition may be illustrated in the transfer matrix $\mathbf{V}$. If we now consider all the q states for each molecule (without reducing them to the two states), $\mathbf{V}$ is a $q \times q$ matrix of the form

$$\mathbf{V} = \begin{pmatrix} a & b & \cdots & b \\ b & c & \cdots & c \\ \vdots & \vdots & \ddots & \vdots \\ b & c & \cdots & c \end{pmatrix}, \tag{A6}$$

where $a = e^{-w/kT}$, $b = e^{-\epsilon/kT}$, and $c = e^{-u/kT}$, both b and c being different from those in the reduced 2×2 matrix (7). In the limit $P \to \infty$ (i.e., $\epsilon \to \infty$), $b = 0$, and so $\mathbf{V}$ is brought to

block-diagonal form. The 4×4 transfer matrix for the one-dimensional KDP model is also of block-diagonal form. On the other hand, in the limit $Q \to \infty$ (i.e., $q \to \infty$), the size of the $q \times q$ matrix becomes infinite in such a way that the ratio of the number of matrix elements that are c to the number that are a or b becomes infinity.

[1] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, Nature (London) **359**, 710 (1992).

[2] S. Iijima, Nature (London) **354**, 56 (1991).

[3] L. D. Gelb, K. E. Gubbins, R. Radhakrishnan, and M. Sliwinska-Bartkowiak, Rep. Prog. Phys. **62**, 1573 (1999).

[4] H. K. Christenson, J. Phys.: Condens. Matter **13**, R95 (2001).

[5] L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part 1* 3rd ed. (Pergamon, New York, 1980), Chap. 8, p. 258.

[6] H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, New York, 1971), p. 2.

[7] K. Morishige and K. Kawano, J. Chem. Phys. **110**, 4867 (1999).

[8] M. C. Gordillo, J. Boronat, and J. Casulleras, Phys. Rev. B **61**, R878 (2000).

[9] H. Kanda, M. Miyahara, and K. Higashitani, Langmuir **16**, 8529 (2000).

[10] K. Koga, G. T. Gao, H. Tanaka, and X. C. Zeng, Nature (London) **412**, 802 (2001).

[11] A. B. Kolomeisky and B. Widom, Faraday Discuss. **112**, 81 (1999).

[12] J. F. Nagle, Am. J. Phys. **36**, 1114 (1968).

[13] G. M. Schütz, I. Ispolatov, G. T. Barkema, and B. Widom, Physica A **291**, 24 (2001).

[14] C. Domb, Adv. Phys. **9**, 149 (1960).

[15] K. Koga, P. Bhimalapuram, and B. Widom, Mol. Phys. **100**, 3795 (2002).

[16] J. C. Slater, J. Chem. Phys. **9**, 16 (1941).

[17] D. Chandler, *Introduction to Modern Statistical Mechanics* (Oxford University Press, New York, 1987), Chap. 5, pp. 155–156.

[18] Y. Takagi, J. Phys. Soc. Jpn. **3**, 273 (1948).