

Melting and surface tension in microclusters

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Approximate partition functions are constructed from approximate quantum mechanical models of near-rigid, solidlike and nonrigid, liquidlike clusters. The Helmholtz free energies are evaluated for these clusters as functions of temperature T and cluster size N . The thermodynamic temperatures of melting, at which the free energies of the two forms are equal, match well with the melting temperatures determined from classical simulations of Ar clusters. Moreover, the effective coexistence ranges of temperature for solid- and liquidlike forms are approximately the same as the range of "supercooling" and "superheating" found in molecular dynamics computations of Ar. The surface tension is determined from an expansion of the free energy in powers of $N^{-1/3}$. The concept of melting in small clusters, as a transition from a near-rigid, small-amplitude vibrator to a nonrigid molecule capable of frequent passage from one local equilibrium geometry to another, is related to the recent proposal by Stillinger and Weber of the nature of the melting transition.

I. INTRODUCTION

The thermodynamics of small clusters of atoms is a venerable subject,¹⁻³ but certain puzzling characteristics of these clusters remain to be interpreted in terms of statistics and thermodynamics. One characteristic is the apparent "melting" of very small clusters that is seen in simulations by both molecular dynamics (MD) and Monte Carlo (MC) computations: clusters of as few as seven argon atoms appear to exhibit sharp transitions between solidlike and liquidlike behavior, and clusters as small as four atoms show both rigid and fluid structures.⁴⁻⁷ Earlier calculations^{8,9} implied a gradual transition between the two forms. The notion of a phase transition in very small systems seems of course to contradict the dogma which requires systems to be made of very many particles indeed in order to show a true sharp phase change. Another characteristic is the emergence of a surface free energy and surface tension as distinguishable properties, when the cluster is so small that it is at least as well considered to be a molecule as it is to be a droplet.

Our purpose here is to show that these two properties, melting and surface tension, can be interpreted rather quantitatively in terms of the statistical thermodynamic properties of very small clusters, with only the weakest, most general assumptions about the specific physical properties of their constituents. In effect, we are addressing the question "How little physics must we put in, in order to understand these two properties in terms of microscopic interaction?" The basis of our reasoning is in the use of approximate, high-symmetry idealizations of the solidlike and liquidlike—or nearly rigid and nearly nonrigid—forms of an N particle cluster. We had used these idealizations previously to construct correlation diagrams relating the energy levels of idealized, nonrigid clusters of N identical particles to those of conventional, nearly-rigid rotator-vibrator hypothetical limiting cases, for a variety of simple molecular systems. In that context, we have been concerned ultimately with the interpretation of high-resolution spec-

tra to infer as much as one can about the nature of the nonrigidity in a molecule. However the calculation that tells one the spacings and degeneracies of the energy levels also tells one the densities of states for the rigid and nonrigid limits. And from these densities of states, one can immediately compute partition functions and all the thermodynamic properties and equilibrium constants for the rigid and nonrigid or, as we shall interpret them, solid and liquid limits.

In the next section we describe the models used to simulate the solid and liquidlike behavior and give explicit expressions for the partition functions of both forms. We also discuss how we chose parameters to minimize their arbitrariness and variability.

The third section presents the calculations of the "melting temperature" curve, the temperature function $T_m(N)$ at which the free energies of solid and liquid forms are equal, as a function of the cluster size. We examine in that section the effective width $\Delta T_m(N)$ of the coexistence region, over which both solidlike and liquidlike forms could be expected to coexist in measurable quantities. The notion of a $\Delta T_m(N)$ is in a sense an arbitrary, heuristic one, but we shall see that its use gives us some insight into the onset of a true first-order phase transition.

That section also deals with the sensitivity of the computations to the assumptions about the characteristic frequencies of the solid and liquid limiting cases and about the degree of idealization or degeneracy of the chosen limiting case. We examine there the severity of assuming, for example, that a simple Einstein model, with its single vibrational frequency, describes the vibrations of the solid form.

The fourth section treats the development of a surface free energy and a surface tension. The results of this calculation are then compared with those of Nishioka,¹⁰ which are based on more detailed and much more system-specific calculations.

Throughout, we use clusters of argon as our model and choose the parameters for our calculations to correspond to Ar-Ar interactions. Because we are trying to compare our results with those of computer simula-

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tions, most of our computations have been done with the same Lennard-Jones interactions used by Briant and Burton,⁴ rather than with the best available Ar-Ar interaction.¹¹

The calculations presented here are a rationalization, not a true explanation, of properties of microclusters. The reason is that one question remains unanswered, namely, "What are necessary and sufficient conditions that, on a scale measuring the degree of rigidity, the free energy of the N -body cluster has two local minima, one near the rigid limit and one near the nonrigid limit?" It is quite conceivable that the free energy of the cluster might have only a single local minimum for a wide variety of conditions, and that such a minimum might occur at any arbitrary point on a scale of rigidity,¹² or even move along that scale as conditions are changed. It is entirely conceivable that the free energy of a cluster could have more than two local minima as a function of its amount of nonrigidity, particularly if the measure of nonrigidity involves more than one parameter. We plan to address this question in a future communication; for the present, we merely postulate the existence of two minima, one in the solidlike and one in the liquidlike region of a generalized rigidity scale.

II. THE CHOICE OF THE MODEL AND ITS PARAMETERS, CALCULATIONS OF THE PARTITION FUNCTION

Let us consider two extremes of dynamical behavior which are assumed to be realizable over some range of temperatures. If the temperature is near 0 K only a few levels just above the absolute minimum of the potential energy are populated. Those levels can be rather accurately calculated by means of a nearly rigid model: the rigid rotor + harmonic oscillators, which is naturally associated with solidlike behavior of a microcluster. Therefore this form is obviously the most stable state of almost all microclusters at low temperatures. We assume that the liquidlike behavior can be described approximately as a nonrigid cluster with pairwise harmonic interactions. With these models, the partition function can be calculated analytically at both limits.

Let us start with the more studied, nearly rigid limit. The partition function of a nearly rigid N -atom cluster is well known.²

$$Q_{\text{rig}} = \frac{\pi^{1/2}}{\sigma} \left(\frac{T}{B}\right)^{3/2} \prod_{j=1}^{\Gamma} \left[\frac{\exp(-\nu_j/2T)}{1 - \exp(-\nu_j/T)} \right]^{\Gamma} \exp(V_e/T), \quad (1)$$

where B is the rotational constant, V_e is the dissociation energy, and ν_j is the energy of the harmonic level spacing of the j th vibrational mode; all energies are in K. The symmetry number σ is introduced to exclude approximately rovibrational levels forbidden by the Pauli principle. Generally it is equal to the number of "feasible" permutations (see Refs. 13, 14, and Appendix A for details). In the particular case of a nearly rigid molecular system the symmetry number coincides with the number of proper rotations in the point symmetry group. For clusters of $N=3$ and 4, we used the correct value of σ ; for larger clusters, the contribution of

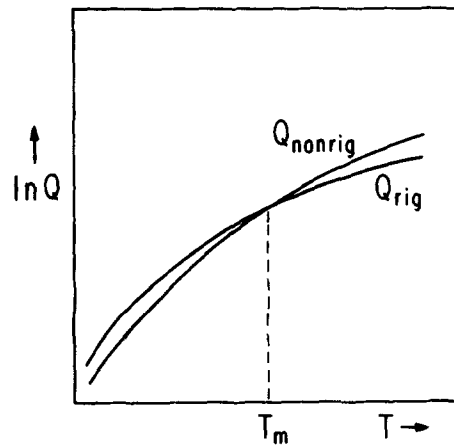


FIG. 1. Schematic showing the crossover point of the nearly rigid partition function and the nonrigid partition function.

σ to the partition function is negligibly small, and we took $\sigma=1$.

At the nonrigid limit any permutation is feasible and hence the symmetry number is equal to $N!$. Therefore one has

$$Q_{\text{nonrig}} = \frac{1}{N!} \left[\frac{\exp(-w/2T)}{1 - \exp(-w/T)} \right]^{3N-3} \exp(V_e'/T), \quad (2)$$

where w and V_e' are again the vibrational frequency and dissociation energy in K.

As the ground state of the nearly rigid microcluster lies near the absolute minimum of the potential energy the dissociation energy of this form into separated particles must obviously be greater than that of the nonrigid cluster and hence the partition function (2) is always less than function (1) at low temperatures. But, with the zero of energy at the ground state of the solidlike cluster, with increasing temperature, the solidlike partition function increases more slowly because the solidlike cluster must surely have higher vibrational frequencies. As a result the difference between the two functions changes its sign at some temperature (see Fig. 1). We identify that point as the thermodynamic melting temperature T_m .

The results of our analysis are somewhat sensitive to the difference in the energies required to dissociate the two forms of the N -atom cluster into N separated particles. Hence these dissociation energies merit some attention. The total dissociation energies of nearly rigid and nonrigid forms are both taken to be proportional to the number $f(N)$ of pairwise nearest neighbor bonds so the ratio of the two dissociation energies is independent of the cluster size. One has

$$V_e = D_e f(N), \quad (3)$$

$$\Delta V_e = V_e - V_e' = x V_e, \quad (4)$$

where D_e and x are independent of N and $f(N)$ is given by a cubic polynomial in $N^{1/3}$ ¹⁵

$$f(N) = 6N - 8.71 N^{2/3} + 2.63 N^{1/3}. \quad (5)$$

The first term is the bulk contribution and the other

terms represent contributions due to the surface, i. e., to atoms with fewer than the maximum number of nearest neighbors. This equation is obtained in Ref. 15 by fitting the polynomial to the two values of $f(N)$ for $N=13$ and $N=767$ given by Abraham.² For $N=19, 43,$ and 55 the values 59.0, 164.7, and 214.0 given by Eq. (5) are also in very good agreement with the accurate ones 60, 164, and 216 taken from Ref. 2.

An analysis of the dissociation energies V_e obtained in Ref. 16 by determination of the structures of minimum potential energy yields a value of D_e in Eq. (3) that is practically independent of N for $13 \leq N \leq 46$. One may then express D_e as

$$D_e = \gamma \epsilon, \quad (6)$$

where ϵ is the well depth for the Lennard-Jones 6-12 potential used in Ref. 16 for a description of the pairwise interaction. If only nearest-neighbor interactions are considered, $\gamma=1$; however the result of Ref. 16 gives $\gamma=1.22 \pm 0.02$, which incorporates non-nearest-neighbor contributions. For $n < 13$, γ takes values between 1 ($N=3, 4$) and 1.22. The dissociation energies of 54 and 64-clusters also calculated in Ref. 16 correspond to $\gamma=1.22$ and 1.16 respectively.

Following Ref. 5, ϵ in Eq. (6) is chosen equal to 120 K and hence $D_e = 146.5$ K. Distributions of vibrational frequencies for the 13-, 19-, 43-, and 55-clusters were taken from Burton's work.¹⁷ The rotational constant B in Eq. (1) is calculated by means of the relation²

$$B = aN^{-5/3}. \quad (7)$$

The constant a is estimated for the icosahedral 13-cluster with one atom in the center and 12 atoms on the sphere of radius $0.966 r_e$,¹⁶ where $r_e = 3.82 \times 10^{-8}$ cm is the equilibrium distance for the Ar-Ar Lennard-Jones 6-12 potential. One finds $a=0.38$ which differs just slightly from the value 0.412 obtained in Ref. 15 for the 3- and 4-atom clusters. It should be stressed that this factor just adds a small additive constant to $\ln Q$, so that there is no particular motivation to determine it more accurately.

Vibrational frequencies of 3- and 4-atom clusters were calculated directly; one also has $V_e = 3\epsilon$ for $N=3$

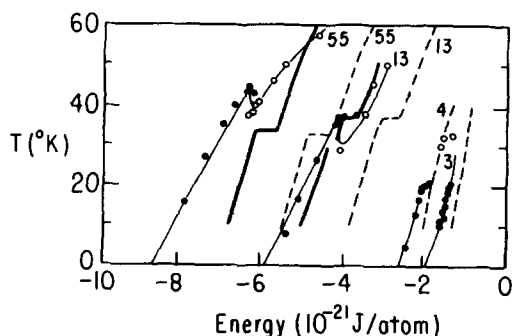


FIG. 2. Mean energies of microclusters as functions of temperature. The thin solid lines represent molecular dynamics results (Ref. 4), the dashed and heavy solid lines represent mean energies obtained by means of our model with $w=10$ K and, respectively, $\alpha=0.11$, $\gamma=1$, and $\alpha=0.09$, $\gamma=1.22$.

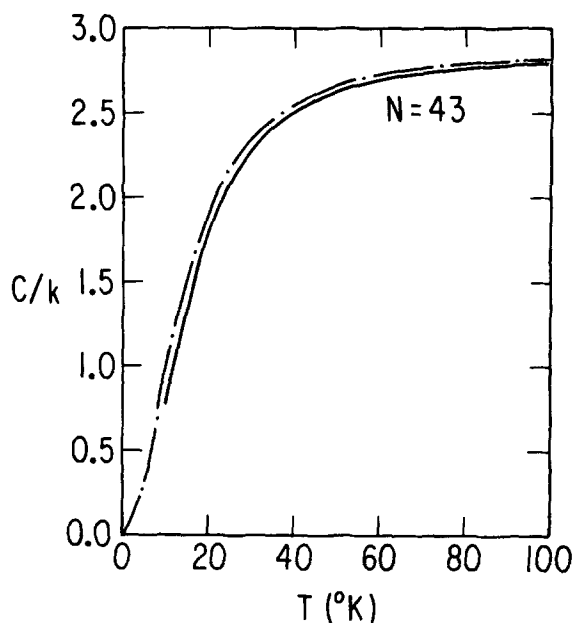


FIG. 3. The heat capacity of the 43-atom solidlike cluster as a function of temperature. The solid line represents our results; the dashed line is taken from Ref. 17.

and $V_e = 6\epsilon$ for $N=4$.

Thus all parameters of the nearly rigid model have been determined and we can compare our calculations of the thermodynamic functions with the results obtained by means of simulations made with classical mechanics.

Figure 2 shows these results for argon clusters in terms of the mean kinetic energy per atom, i. e., temperature, as a function of total energy per particle. The heavy solid and dashed curves were computed from the partition functions, with the rigid-limit function below the transition temperature T_m and the nonrigid-limit function above. The coexistence ranges are shown by the horizontal sections of the curves, which are drawn at T_m with widths determined directly from the difference in the free energies at T_m . The simulations in this figure, shown by light lines, are those of Briant and Burton.⁴ Our results are given for $\gamma=1$ and $\gamma=1.22$. Both give the same shapes as the simulations, but correspond to different locations on the abscissa.

Comparing parts of the curves below the breaks in Fig. 2 one can conclude that taking into account long-distance interaction implicitly by choosing $\gamma > 1$ improves agreement with classical calculations of the mean energy.⁴ The shifts still left are caused mainly by the zero-point vibrations which are neglected in the classical calculations. Note that the slopes of all the curves for the nearly rigid case are approximately the same. In fact, the vibrational heat capacity per atom given by Burton¹⁷ for the 43-atom cluster is in very good agreement with our calculations (Fig. 3) at the nearly rigid limit.

The curves in Fig. 4 represent the Helmholtz free energies $A(N)$ calculated by us at this limit and obtained by means of classical normal mode approach.¹⁸ Again the differences between those curves are caused mainly

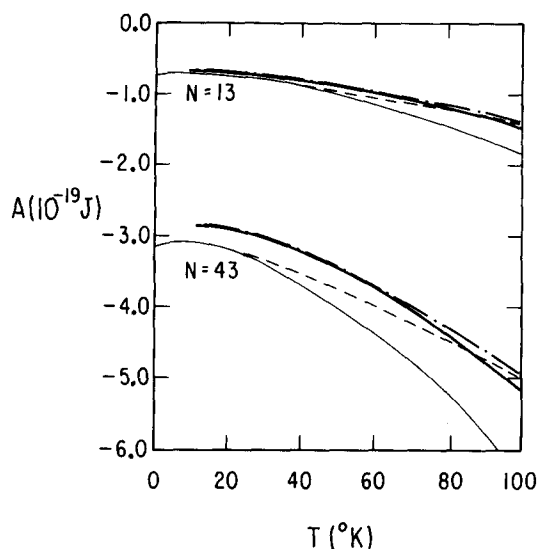


FIG. 4. The Helmholtz free-energy as a function of temperature. The heavy and thin solid lines correspond respectively to our solid-plus-liquid model and to Monte Carlo simulation (Ref. 18). The heavy and thin dashed lines represent, respectively, our normal mode calculations for solid clusters with the classical ones (Ref. 18).

by the neglect of the zero-point vibrations in the classical calculations. As expected, those differences decrease as temperature increases.

At this point we have only two parameters; w , the vibration frequency of the nonrigid form and x the scaled well depth, both of which vary. Their choice is discussed in the next section.

III. THE MELTING TEMPERATURE AND ITS SENSITIVITY TO DISTRIBUTION OF VIBRATIONAL FREQUENCIES AT THE NEARLY RIGID LIMIT

In order to find parameters x and w , we made use of the results of molecular dynamics simulation⁴ for the melting temperature and entropy change of 12- and 55-atom clusters [see the columns (I) in Table I]. The entropy change ΔS is calculated by means of the relation

$$\Delta S = \Delta E / T_m, \quad (8)$$

where ΔE is the difference between mean energies per atom

$$E_i = \frac{T^2}{N} \frac{\partial}{\partial T} \ln Q_i \quad (9)$$

of the nonrigid and nearly rigid clusters at the melting temperature. We found $w = 10$ K and $x = 0.09$.

The coexistence range is defined in a purely heuristic way as the temperature interval within which

$$0.1 < \frac{Q_{\text{rig}}}{Q_{\text{nonrig}}} < 10. \quad (10)$$

Its width ΔT decreases rather rapidly as the cluster size increases.

Note that all those quantities: the melting temperature, entropy change, and coexistence range depend only on the difference between the dissociation energies at both limits, i. e., on the product xy . Hence their dependence on the cluster size does not change if one puts y just equal to 1 and slightly increases x . For example, the dashed ($x = 0.11$, $y = 1.0$) and heavy solid lines ($x = 0.09$, $y = 1.22$) break at the same temperature making the same discontinuous change.

TABLE I. Different melting characteristics obtained by means of our model and molecular dynamics simulation. The quantities in the three sections are the melting temperature T_m , the entropy of melting (ΔS) and the effective coexistence range ΔT . The columns labeled (I), (II), and (III) were calculated using, respectively, the real distributions of nearly-rigid vibrational frequency, the single frequency dependent of N according to Eq. (11) and the single N -independent frequency $\bar{\nu} = 52$ K. The columns marked by BB and EK are taken, respectively, from Refs. 4 and 7. The width of van der Waals loops observed in molecular dynamics results (Ref. 4) was treated as the width ΔT of the proper coexistence range.

	(I)	(II)	(III)	BB	EK	(I)	(II)	(III)	BB	(I)	(II)	BB
			$T_m(\text{K})$					$\Delta S/k$			$\Delta T(\text{K})$	
3	>100			...	13.3							
4	64			~20.6	...	0.6			~1.2			2.5
5	...	53		~22.6	15.7		...	0.6	~1.2		...	1.2
6	...	31		~20	9.6		...	0.9	~1.2		...	5
7	...	22		20	15.7		...	0.8	1.2		...	1.2
13	38	39	< 5	35	28.75	0.8	0.8	...	1.0	16.5	19	7
19	36	32	< 5			0.9	1.2	...		9.5	9	
35		31	21	38			1.3	0.8	0.8		5	3.5
43	38	33	26			0.9	1.3	1.1		4	4	
55	32	37	33	40		1.0	1.2	1.3	0.6	3	3.5	6
100		55	62	41			0.7	0.3	0.8		3.5	3.5

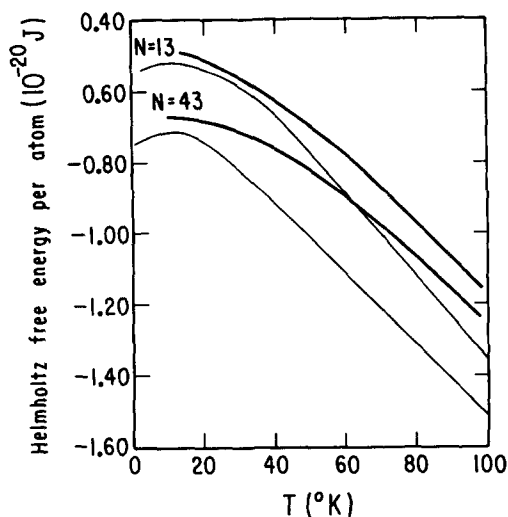


FIG. 5. The Helmholtz free energy per atom as a function of temperature. The heavy and thin solid lines correspond respectively to our solid-plus-liquid model and to Monte Carlo simulation (Ref. 18).

The solid curves in Figs. 4 and 5 represent our calculations of the Helmholtz free energy and the Helmholtz free energy per atom for the combined nearly rigid-non-rigid model compared with the results obtained by Monte Carlo method.¹⁸

The columns (II) and (III) in Table I are obtained by means of the Einstein model with only a single vibrational frequency at each limit. They differ from each other by dependence of the vibrational frequency $\bar{\nu}$ of the solidlike cluster of N . The N -dependent frequency (the columns II) is defined by the relation

$$\bar{\nu}(N) = 61 + 0.88N^{-1/3} - 221.9N^{-2/3} + 249.4N^{-1} \text{ (K)}, \quad (11)$$

where the first term corresponds to an infinite crystal¹⁹ and the next coefficients of the expansion in $N^{-1/3}$ are obtained by a fit to the mean frequencies of the 13-, 19-, 43-, and 55-solidlike clusters. Parameters $w = 11.2$ K, $\alpha = 0.08$ are chosen based on the results of molecular dynamics simulation⁴ for 13-, 33-, and 55-atom clusters. The columns (III) in Table I were obtained using the same values of parameters w and α but the vibrational frequency at the nearly rigid limit was made independent of the cluster size and set equal to 52 K. Increasing $\bar{\nu}$ to make the melting temperature higher

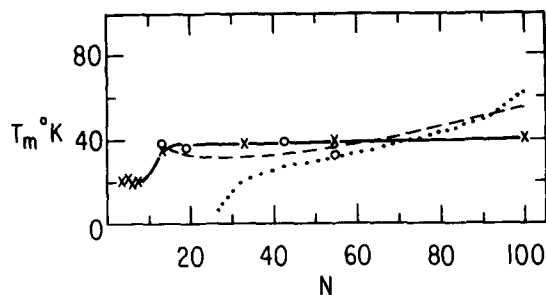


FIG. 6. Effect of the form of frequency on the melting temperature. The solid line goes through the molecular dynamics points (Ref. 4) marked by crosses. The circles correspond to our points based on the "real" distributions (Ref. 4) of nearly rigid vibrational frequencies. The dotted line corresponds to the Einstein model with a single N -independent frequency at each limit and the dashed line represents calculations making the single nearly rigid vibrational frequency dependent on N according to Eq. (11).

leads to the unrealistic picture for the 100-atom cluster in which "melting" becomes an exothermic process.

As one can see from Table I and Fig. 6, the Einstein model with a single N -independent vibrational frequency at each limit leads to too rapid change of the melting temperature as a function of N and no variation of parameters w and α resolves this problem.

Making the vibrational frequency of the solidlike cluster dependent of N brings the model into much better agreement with the melting temperatures obtained from molecular dynamics, except that molecular dynamics simulation⁴ predicts a monotonic increase of the melting temperature as the cluster size increases at least from 13-100.

It should be pointed out that the melting temperature is very sensitive to the distribution of vibrational frequencies. The fact that the spread of the values of T_m is so narrow for the realistic frequency distributions strongly supports the model.

Table II illustrates the sensitivity of the calculated characteristics to the choice of parameters. Note that the use of the realistic distribution of frequencies ν_j , instead of a single $\bar{\nu}(N)$ leads to a broader coexistence range, to melting at higher temperatures and to lower heats of fusion.

TABLE II. Sensitivity of the melting temperature to a variation of parameters. The function $\bar{\nu}(N)$ is determined by Eq. (11).

N	$\nu_j = \bar{\nu}(N)$											
	The distribution of frequencies ν_j from Ref. 4.											
	$w = 10 \text{ K}, \alpha = 0.09$			$w = 10 \text{ K}, \alpha = 0.09$			$w = 10.5 \text{ K}, \alpha = 0.09$			$w = 10 \text{ K}, \alpha = 0.10$		
	T_m K	ΔS /K	ΔT K	T_m K	ΔS /K	ΔT K	T_m K	ΔS /K	ΔT K	T_m K	ΔS /K	ΔT K
13	31.5	1.2	11.5	38	0.8	16.5	45	0.8	22	43	0.9	18
19	29	1.6	7	36	0.9	9.5	42	0.8	12.5	41	1.0	10.5
43	30	1.6	3	38	0.9	4	44	0.9	5.5	43	1.0	4.5
55	27	1.6	2	32	1.0	3	37	0.9	3	37.5	1.1	3

Increasing w obviously decreases the partition function of a nonrigid cluster and hence leads to higher melting temperatures. By analogy, increasing x raises the bottom of the nonrigid well and also increases melting temperatures. In both cases, increasing w or x , the coexistence range is broadened but their effects on the entropy change are opposite: increasing w decreases the entropy of melting whereas increasing x decreases that entropy change.

IV. SIZE DEPENDENCE OF THE SURFACE TENSION

It is essential that the nonrigid limit makes it possible to describe the surface tension—a very important characteristic of a liquid droplet. Following Nishioka¹⁰ we calculate the surface tension γ by means of the equation

$$\gamma(N) = -\frac{R_{cl} N}{v_e} \frac{\partial [A(N)/N]}{\partial N}, \quad (12)$$

where R_{cl} is the radius of the cluster, v_e is the volume per atom in the bulk liquid, i. e.,

$$\frac{4}{3} \pi R_{cl}^3 = N v_e. \quad (13)$$

Both Helmholtz free energy per atom $A(N)/N$ and surface tension $\gamma(N)$ must tend to constants as N tends to infinity. Taking into account Eq. (12) and Eq. (13) one can conclude that the function $A(N)/N$ is represented at large N as

$$A(N)/N = f_\infty + C_1 N^{-1/3} + O(N^{-2/3}), \quad (14)$$

where the coefficient C_1 is connected with the surface tension γ_∞ of bulk liquid by the relation

$$C_1 = \gamma_\infty \sqrt[3]{4\pi(3v_e)^2}. \quad (15)$$

Deducing the Helmholtz free energy per atom for the bulk liquid from the simulation data²⁰ Nishioka¹⁰ estimated the first term in the expansion (14) as

$$f_\infty \times 10^{13} = -1.45 \text{ to } -1.57 \text{ erg} \quad (16)$$

at temperatures increasing from 70–84 K. Then he fitted the function $A(N)/N$ to the cubic polynomial in $N^{-1/3}$:

$$A(N)/N = f_\infty = C_1 N^{-1/3} + C_2 N^{-2/3} + C_3/N, \quad (17)$$

using the data from the Monte Carlo calculations^{18,21} of the internal Helmholtz free energy which were found²¹ by subtracting the rotational free energy from the total, for clusters with centers of mass fixed in space. He obtained the following estimates for the coefficients:

$$\begin{aligned} C_1 &= 1.4 \text{ to } 1.1 \times 10^{-13} \text{ erg}, \\ C_2 &= -0.73 \text{ to } -0.36 \times 10^{-13} \text{ erg}, \\ C_3 &= 1.9 \text{ to } 2.1 \times 10^{-13} \text{ erg}, \end{aligned} \quad (18)$$

at temperatures increasing, as previously, from 70–84 K. Substituting Eq. (17) into Eq. (12) Nishioka estimated the coefficients in the expansion

$$\gamma(N) = \gamma_\infty + D_1 N^{-1/3} + D_2 N^{-2/3}, \quad (19)$$

as

$$\begin{aligned} \gamma_\infty &= 23 \text{ to } 18 \text{ dyn/cm}, \\ D_1 &= -24 \text{ to } -12 \text{ dyn/cm}, \\ D_2 &= 95 \text{ to } 100 \text{ dyn/cm}. \end{aligned} \quad (20)$$

The nonrigid limit under consideration leads to the expression for the Helmholtz free energy per atom:

$$A(N)/N = -kT \left[\left(3 - \frac{6}{N} \right) q + (1-x) \frac{D_e}{T} f(N)/N + 1 - \ln N \right], \quad (21)$$

which is rather close to Eq. (17), except for the logarithmic term, as q is independent of N :

$$q = -\frac{w}{2T} - \ln(1 - e^{-w/T}) \quad (22)$$

and $f(N)$ is determined by Eq. (5). The fact that we include rotations does not seem essential as their contribution to the partition function appears to be negligible. Note that the expression for the vibrational Helmholtz free energy of the solidlike cluster exactly coincides with Eq. (17)¹⁵ and the proper coefficients (as also shown by Amar¹⁵) are close to Eqs. (16) and (18). The coefficients f_∞ and C_3 determined from Eq. (21) are not particularly sensitive to the value of the vibrational frequency; C_1 and C_2 are altogether independent of it. Hence, Amar's results could be extended to the nonrigid limit except that $N!$ appears in the partition function of the liquid cluster. It would be wrong to infer from this that our model of a liquid droplet leads to wrong results, because the formula (2) is only asymptotic in N and therefore is not valid as $N \rightarrow \infty$. Hence, Eq. (21) cannot be treated as an expansion at large N .

In order to estimate the coefficients C_i in the free energy, we fitted the polynomial in Eq. (17) to data obtained by us for 13-, 19-, 43-, and 55-atom nonrigid clusters, taking for f_∞ the values given by Nishioka.¹⁰ At temperature 80 K we found

$$\begin{aligned} C_1 &= 3.7 \times 10^{-13} \text{ erg}, \\ C_2 &= -10.3 \times 10^{-13} \text{ erg}, \\ C_3 &= 11.3 \times 10^{-13} \text{ erg}. \end{aligned} \quad (23)$$

The fact that we obtained correct signs of those coefficients (especially the first one, whose sign coincides with the sign of γ_∞ and hence must be positive) seems rather reassuring as even the signs are very sensitive to variations of the fitted values. Moreover one should not forget that we used only four points to find three coefficients, i. e., significant errors of fitting are expected. In fact, if we put $C_3 = 0$ and fit the cubic polynomial to the same data the results agree much better with Nishioka's results

$$\begin{aligned} C_1 &= 2.4 \times 10^{-13} \text{ erg}, \\ C_2 &= -2.5 \times 10^{-13} \text{ erg}. \end{aligned} \quad (24)$$

Substituting Eq. (17) into (12) and using the values in Eq. (24) of the coefficients C_i we obtain for the surface tension the following estimation:

$$\begin{aligned} \gamma_\infty &= 40 \text{ dyn/cm}, \\ D_1 &= -65 \text{ dyn/cm}, \end{aligned} \quad (25)$$

at 80 K. For such a simple model, the agreement seems quite satisfactory especially taking into account what high-order quantities we try to extract.

Therefore we can conclude that the nonrigid limit in question does describe the main properties of a liquid

droplet, qualitatively and even to correct magnitudes.

The approach taken here is based on a microscopic, i. e., molecular, quantum-mechanical picture of the small cluster and asks how surfacelike terms emerge in the free energy from such a model as a result of the distribution of numbers of nearest neighbors and the distribution of vibrational modes. The questions addressed in this way should be distinguished from the complementary viewpoint taken recently by Sinanoğlu^{22, 23} who has used smooth distributions appropriate to classical models and to clusters large on the scale of this discussion, in order to show how surface characteristics develop as clusters grow.

V. CONCLUDING REMARKS

The models of a liquid cluster as a nonrigid molecule and a solid cluster as a conventional nearly rigid molecule contain, as we have seen, enough reality to give encouraging replication of classically computed melting points, coexistence ranges and surface tension of those same clusters. There are a few molecules known to be nonrigid even in their ground states: the isosceles-triangular triatomic alkalis are examples. Yet even these molecules seem to be describable in terms of adiabatic potential surfaces. The motions of the atomic nuclei in such molecules have amplitudes comparable with the distances between one potential minimum and another physically equivalent minimum, rather than the usual, much smaller amplitudes.

There are two points to be made concerning these large-amplitude, nonrigid motions. One concerns the nature of nonrigidity in a quantum-mechanical system; the other is a speculation that relates our work to recent simulations of the melting transition.

Motions in nonrigid systems are sometimes taken to be associated with violations of the Born–Oppenheimer or adiabatic approximation. It is true that such violations are sometimes found in systems with large-amplitude motions, especially when those motions carry the nuclei to configurations where adiabatic surfaces cross. However it is important to recall how the Born–Oppenheimer approximation and the small-amplitude oscillation model became entangled. The method used by Born and Oppenheimer was a paradigm of the use of Rayleigh–Schrödinger perturbation theory in which the zeroth order gave rise to the effective potential energy surface and the second order led directly to the picture of harmonic, small-amplitude oscillations on that surface. The first is quite a separate matter from the second. It is quite possible for a molecule to exhibit *adiabatic* nonrigidity, provided the electronic wave function adjusts rapidly to every new configuration of the nuclei, even when the nuclear motions cover large amplitudes. There appears to be no intrinsic problem with the idea of a single adiabatic potential surface with many minima, to describe the motions of atoms in a liquid cluster as a nonrigid molecule, or the motions of the atoms of a bulk liquid in terms of passage by large-amplitude motions from a region around one potential minimum to a region around another nearby minimum.

This brings us directly to the second point, because the model of a liquid as a system passing from a region around one potential minimum to another is precisely the picture that Stillinger and Weber^{24, 25} have presented for a liquid, based on their classical-mechanical simulations of a two-dimensional, Gaussian-repulsion system. By “cooling” they have identified the metastable equilibrium configuration about which their system was oscillating at the moment that isothermal mechanical motion was replaced by a quenched descent to the lowest monotonically available energy. The equilibrium configurations they find are essentially defective ordered solids with grain boundaries, dislocations or both. What is relevant to this discussion is that in the Stillinger–Weber picture and in our conception of clusters, the solid form is locked into small-amplitude vibrations about a single configuration for a time that is effectively infinite, while the liquid form passes by large-amplitude motion from one minimum to another that is equivalent, as in pseudorotation, or negligibly different, as in motion of a grain boundary.

In the “solid” cluster with finite barriers between one potential minimum and another, the time of passage between these minima is of the order of the splitting of the stationary states associated with tunneling between minima. In molecules ordinarily considered rigid, even in ammonia with its inversion motion, these passage times are comparable to or slower than typical rotational frequencies and are much slower than the atomic vibrational frequencies.

In a nonrigid molecule or cluster, this separation of time scales is no longer valid. Rather, the frequencies of passage from one minimum to another may merge smoothly into the range of ordinary bending or torsional vibrations. An example that seems trivial in the present context is the broad range of periods of torsional motion, ranging from essentially free internal rotation in CH_3NO_2 to the almost pure, small-amplitude torsional oscillations of substituted ethanes. It is natural to conjecture at this point that *the melting transition is characterized specifically by the breakdown in the separation of time scales* for small-amplitude vibrations within the regions around effectively equivalent potential minima, and for the large-amplitude motions that connect them.

Stillinger and Weber^{24, 25} have already pointed out that their simulations implicate large-amplitude motions as playing an important role in the dynamics of liquids. If our conjecture is correct, then molecular dynamics simulations of “bulk” liquids carried out with the “quenching” procedure of Stillinger and Weber should show that the grain boundaries and dislocations of the equilibrium configurations move on a time scale roughly comparable to that of the small-amplitude vibrations. That is, the bulk system should pass among its potential minima at a rate not much slower than its rate of binary collisions. If computations confirm this conjecture we can begin to identify with some confidence the transition from rigid-to-nonrigid cluster as the microscopic expression of true melting.

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APPENDIX A: THE SYMMETRY NUMBER

Let us start with the general definition of the partition function

$$Q = \sum_j g_j \exp(-E_j/T), \quad (\text{A1})$$

where g_j and E_j are the nuclear statistical weight and energy of the j th level. In the general case eigenfunctions corresponding to those levels are determined only in a domain separated from the rest of nuclear configurational space by a rather high barrier. Permutations and permutation inversions which convert this domain onto itself are called "feasible"²⁶; the group which they form is called the Longuet-Higgins group or the Q group. It is essential that the eigenfunctions corresponding to the same energy must span a representation of this group. As far as our aim is just to calculate the statistical weights, only its subgroup formed by pure permutations (not followed by inversion) is required. Using Frobenius' theorem (see Ref. 27 for details) one can easily prove that the statistical weight is equal to the number of wave functions totally symmetric for bosons and antisymmetric for fermions under the mentioned subgroup (of course, a spin part of each wave function must be also taken into account). The statistical weights can be calculated using standard algorithms of the group theory.^{27,28} But here we are interested only in the very particular case in which

spinless eigenfunctions corresponding to a degenerate or quasidegenerate level span a representation whose characters are equal to zero for every feasible permutation, except of course the identity. We shall call this the multiple-regular representation as it can be decomposed into a sum of representations equivalent to the regular representation. The number of times each (i th) representation occurs in the decomposition of the multiple-regular representation into irreducible ones is

$$f_i^p = \frac{l_i d_p}{g} \equiv l_i p, \quad (\text{A2})$$

where l_i is the dimensionality of the i th irreducible representation, p and d_p are the multiplicity and dimensionality of the multiple-regular representation, g is the order of the group under consideration. Note that an arbitrary (to say p -fold) multiple-regular representation is a multiple-regular representation of any subgroup of the mentioned group. Its multiplicity is d_p/h , where h is the order of the subgroup.

If high excited states of a molecular system span multiple-regular representations the proper statistical weights can be found easily: for N identical particles with spin s

$$g_j = (d_j/\Sigma) (2s+1)^N, \quad (\text{A3})$$

where Σ is the number of feasible permutations. As proved in Ref. 28 (see also Ref. 29) a representation spanned by wave functions of a symmetric top asymptotically tends to a multiple-regular representation as total angular momentum tends to infinity. Hence, one can conclude that any representation spanned by rovibrational wave functions also asymptotically tends to a multiple-regular one whatever is the symmetry of the vibrational state in question because the product of a multiple regular representation and, an arbitrary representation is again a multiple regular representation. Therefore, the error due to the replacement of accurate sta-

TABLE III. Ratio of the accurate value of the statistical weight and its asymptotic estimate for different excited states and numbers of atoms.

$j \backslash N$	3	4	5	6	7	8	9	10
2	1.71	3.2	9.2	36	177	1047	7257	57600
3	1.07	1.45	3.3	10.6	44	228	1396	9931
4	1.00	1.75	3.2	8.5	30	137	744	4767
5	1.07	1.12	2.2	5.0	15.5	61	299	1730
6	1.08	1.39	1.95	4.3	11	40	175	917
7	0.95	1.09	1.67	3.0	7.6	24	93	443
8	1.06	1.21	1.55	2.7	5.9	17	60	263
9	1.00	1.05	1.41	2.2	4.6	12	39	154
10	1.00	1.13	1.35	2.0	3.8	9.1	27	100
11	1.01	1.03	1.27	1.80	3.2	7.0	19	66
12	1.02	1.09	1.23	1.69	2.8	5.8	15	46
13	0.99	1.02	1.19	1.56	2.5	4.8	11	33
14	1.02	1.06	1.17	1.49	2.2	4.1	9.1	25
15	1.00	1.02	1.14	1.41	2.0	3.5	7.5	19
16	1.00	1.04	1.12	1.36	1.89	3.1	6.3	15
17	1.00	1.01	1.11	1.31	1.77	2.8	5.4	12
18	1.00	1.03	1.10	1.27	1.67	2.6	4.7	10
19	1.00	1.01	1.08	1.24	1.59	2.4	4.1	8.5

tistical weights by their asymptotic estimates depends only on the ratio of temperature and rotational constant, i. e., it is independent of vibrational frequencies, at least until the quasirigid approach is applied.

We could not prove that the representations spanned by eigenfunctions of the isotropic oscillator tend to a multiple regular representation as the number of vibrational quanta increases. But our calculations carried out for the totally symmetric representation of the full permutational group (see Appendix C), i. e., for spinless bosons support the asymptotic formula (A3) at least in this case.

APPENDIX B: THE RANGE OF APPLICABILITY OF THE ASYMPTOTIC ESTIMATION FOR THE PARTITION FUNCTION AT THE NONRIGID LIMIT

The formula (A3) is actually fulfilled, if at all, only in an asymptotic sense for $j \gg N$ and can be used for the calculation of the partition function provided the proper states mainly contribute to the series (A1). In order to estimate those terms we use Stirling approximation for j -dependent factorials in the expression

$$d_j = \frac{(3N - 4 + j)!}{j! (3N - 4)!} \tag{B1}$$

for the degeneracy of the j th level. Putting

$$a_j = g_j \exp(-jw/T), \tag{B2}$$

one finds

$$\ln a_j \approx -\frac{jw}{T} + (3N + j - 3.5) \ln(3N + j - 4) - (j + \frac{1}{2}) \ln j + C(N), \tag{B3}$$

where

$$C(N) = -(3N - 4) - \ln[(3N - 4)! N!]. \tag{B4}$$

Differentiating (B2) with respect to j we obtain that the terms a_j in the partition function reach the maximum value a_{max} at

$$j_0 \approx 3N - 4/e^{w/T} - 1 \tag{B5}$$

at least if the asymptotic estimations (A3) are applied for the statistical weights. Substituting (B5) into (B3) one has

$$\ln a_{max} \approx -(3N - 4) \ln(1 - e^{-w/T}) - \frac{1}{2} \ln(3N - 4) - \ln N! \tag{B6}$$

and hence, for $N \gg 1$ terms near the maximum have the same order of magnitude as the whole sum.

Now we are ready to obtain an upper bound for N based on the obvious inequality

$$a_{max} \gg 1, \tag{B7}$$

which means that terms near the maximum must be much greater than the first term in the partition function. Taking the logarithm of both sides of inequality (B7), substituting Eq. (B6) and using Stirling approximation for $N!$ one finds

$$1 + (3w/T) > \ln[N(e^{w/T} - 1)^3]. \tag{B8}$$

[The replacement of "much greater" by "greater" becomes possible after dividing the inequality (B7) by N .]

After simple transformations one has

$$N < e(1 - e^{-w/T})^{-3}. \tag{B9}$$

For $w = 10$ K and $T \sim 30$ K the cluster size must be no greater than $N = 119$. Actually we found just an upper bound and real numbers of atoms in a cluster must be even smaller. See Table III.

In fact, the partition function (A1) with $E_j = jw$ is expected to increase as the cluster size grows. Our accurate calculations of the statistical weights of spinless bosons for $j < 20$ (see Appendix C) do support these expectations: for any fixed value of j under consideration the statistical weight increases as the cluster size grows from 1 to j . For $N \geq j$ it is independent of N (see the proof in Appendix C). Therefore one can conclude that the accurate partition function (even if energy levels are referred to the ground state) does monotonically increase as N increases whereas its asymptotic estimation reaches its maximum value at

$$N_0 = (1 - e^{-w/T})^{-3} \tag{B10}$$

i. e., e times less than the upper bound in inequality (B9). For $w = 10$ K and $T \sim 30$ K $N_{nonrigid}$ has the maximum at $N \approx 43$. Actually the asymptotic formula (2) for the partition function can be applied for slightly larger values of N

$$\Delta N \equiv N - N_0 \ll N, \tag{B11}$$

as one can neglect the error compared with the value of the partition function. Taking into account that the second derivative of $\ln Q_{nonrigid}$ with respect to N is equal to $-1/N$ one can estimate this error and, as a result, the sensitivity of the found values of the melting temperature to this error. One has

$$-\frac{1}{2} \frac{\Delta N^2}{N} \approx 3N \frac{w \Delta T}{T^2} (e^{w/T} - 1)^{-1} \tag{B12}$$

or

$$\Delta T \approx -\frac{1}{6} \left(\frac{\Delta N}{N}\right)^2 \frac{T^2}{w} (e^{w/T} - 1). \tag{B13}$$

Putting $T = 30$ K, $\Delta T = 0.5$ K, $N = 43$, and $w = 10$ K, we can estimate ΔN as $\Delta N \sim 12$ and hence the asymptotic formula (2) can be applied at 30 K only for $N \leq 55$. Therefore the 55-atom cluster is very close to the bound where Eq. (2) is no longer valid. However, it should be stressed that the range of applicability widens very rapidly as temperature increases. For example, at $T = 32$ K, the estimation (B10) gives $N_0 \approx 51$ and the use of Eq. (2) for $N = 55$ leads to the very small error $\Delta T \sim 0.05$ K in the calculations of the melting temperature (the error in the estimations of the coexistence range is obviously greater).

It is easily verified that the condition $j_0 \gg N$ is fulfilled automatically.

APPENDIX C: THE ALGORITHM FOR CALCULATING THE STATISTICAL WEIGHTS OF SPINLESS BOSONS

Let $u_{\mu x}$ ($\mu = 1, 2, \dots, N - 1$) be a coordinate describing the μ th normal vibration along the X axis. The coordinates $u_{\mu x}$ span the irreducible representation $(N - 1, 1)$

of the symmetric group S_N realized by permutations of the Cartesian coordinates r_{ix} of atoms. By analogy, coordinates u_{iy} and u_{iz} are introduced.

The harmonic functions corresponding to any energy level at the nonrigid limit span the symmetrized Kronecker power representation of the unitary group $U(3N-3)$. Our aim is to calculate the number of the functions which are totally symmetric under permutations of atoms. The general formula for this calculation is well known³⁰ but it is based on functions of all possible partitions of an integer and one needs very bulky arrays to keep such information. That is why we choose another way.

Let us consider the symmetrized Kronecker power representation of the unitary group $U(3N)$, the representation generated by the Cartesian coordinates of atoms. Because coordinates of the center of mass belong to the totally symmetric representation of the symmetric group S_N one can express symmetrized homogeneous polynomials of r_{ix} , r_{iy} , r_{iz} as a linear combination of homogeneous polynomials of u_{ix} , u_{iy} , u_{iz} having the same symmetry (the coefficients are homogeneous polynomials of the coordinates of the center of mass). Therefore we find

$$L_j^{(3,N)} = \sum_{j'} \binom{j-j'+2}{2} g_{j'}^{(3,N)}, \quad (\text{C1})$$

where $L_j^{(3,N)}$ and $g_j^{(3,N)}$ are the numbers of symmetrized homogeneous polynomials of the variables r_{ix} , r_{iy} , r_{iz} and u_{ix} , u_{iy} , u_{iz} , respectively, for the symmetry type in question. We omit the subscript corresponding to the symmetry type just because we are interested here only in the totally symmetric representation.

If all the numbers $L_j^{(3,N)}$ have been known, one can find $g_j^{(3,N)}$ treating (C1) as a recurrence formula. We prove that $L_j^{(3,N)}$ is the number of all possible partitions of j into not more than N triads. Each triad contains one positive and two nonnegative integers arranged in order; the arrangement is essential. Each partition determines the subspace of monomials (products of j Cartesian coordinates) which is invariant under permutations of atoms and contains a single totally symmetric polynomial with unit coefficients.

We use the term "length of triad" for a sum of the three integers forming the triad given. Denoting the number of partitions of μ into not more than \mathcal{K} triads of length $< p$ by $l_{\mu,p}^{(3,\mathcal{K})}$ one has

$$l_{j,p+1}^{(3,N)} = \sum_{k=0}^K \binom{m_p+k-1}{k} l_{j-pk,p}^{(3,N-k)}, \quad (\text{C2})$$

where m_p is the number of different triads of length p , i. e.,

$$m_p = \sum_{p'=0}^p (p-p'+1) = (p+1)(p+2)/2. \quad (\text{C3})$$

As a result we find

$$L_j^{(3,N)} = l_{j,j+1}^{(3,N)}. \quad (\text{C4})$$

The relations (C1)–(C4) allow one to calculate the statistical weights $g_j^{(3,N)}$ for different j and N . Note that statistical weights $g_j^{(3,N)}$ are independent of N if $N > j$.

Equation (C1) represents the ratio of the accurate value of the statistical weight $g_j^{(3,N)}$ and its asymptotic estimation as a function of j and N for $j, N < 20$. One can conclude that the ratio does tend to 1 as j increases to become much greater than N . Note that this ratio is generally more than 1, i. e., the asymptotic formula undervalues the partition function and hence overestimates the melting temperature.

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