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Cluster free energy in the simple-cubic Ising model

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The Monte Carlo technique previously developed to compute directly the free-energy difference between two clusters containing $N+1$ and N particles is applied to the three-dimensional cubic Ising model with nearest-neighbor interactions. For cluster sizes $1 \leq N \leq 19$, at two reduced temperatures ($T/T_c = 0.4$ and 0.59) it is found that down to surprisingly small sizes ($N \geq 8$) the free energy F_N can be written as $F_N = Na + N^{2/3}b + N^{1/3}c + d + \tau\beta^{-1}\ln N$, where a and τ are given their theoretical value for bulk phases, and b, c, and d can be understood, respectively, as the surface contribution, a step contribution, and a vertex contribution. A Fisher-type model ($F_N = Na + N^{\sigma}\Sigma + \tau\beta^{-1}\ln N$) when fitted to the data yields a size- and temperature-dependent value of σ. Other proposed models are shown to depart systematically from our data. Typical values of nucleation rates for this model, as predicted from the present data, range from 10^{-3} to 10^{+2}—those expected from the classical capillarity approximation of F_N.

I. INTRODUCTION

It has long been recognized that the nucleation rate in first-order phase transitions is extremely sensitive to the free energy of the nucleus and especially to the interfacial energy between the dense and dilute phase.[1] The nucleus free energy is classically evaluated following the capillarity approximation, considering the nucleus as a macroscopic drop, the free energy of which is the sum of a bulk and of a surface contribution, the energy per bulk or surface particle being set equal to their macroscopic value. This procedure has often been questioned (for a review see Ref. 2) and various expressions have been proposed for the free energy of the nucleus: Let us quote the Lothe-Pound correction,[3] the use of Fisher's droplet model,[4–6] the inclusion of curvature effects on surface free energy (e.g., Refs. 7 and 8) among other more empirical approaches.

In view of the experimental difficulty for studying the thermodynamical properties of small aggregates, the knowledge one has of such properties often results from fitting the nucleation rate, as predicted by the classical Becker-Döring theory to experimentally measured rates. This procedure is quite common in physical chemistry[6,7,9,10] as well as in physical metallurgy.[11] Since one of the major interests of knowing nuclei properties would be to predict or at least to rationalize nucleation rates, the above procedure is not very satisfactory. Moreover, the Becker-Döring theory rests on many intuitive assumptions, the range of validity of which is not well defined.[12]

A better knowledge of nuclei properties is certainly desirable. Several theoretical attempts have been made to predict the energy of nuclei.[13] In view of the many difficulties inherent to this problem, some attempts have been made to measure the free energy of clusters (the quantity which really matters in the rate of nucleation) in model systems amenable to computer simulations: clusters of Lennard-Jones atoms, the dynamics of which were generated by molecular dynamics,[14] clusters in the Ising model, configuration space of which was explored by a Monte Carlo technique.[15,16]

As is well known, however, free energy cannot be measured directly and must be obtained by integration of another thermodynamic quantity along the proper path. Such a procedure is therefore too heavy to allow systematic studies with the high precision required to discriminate between conflicting models of nuclei.

In a previous paper,[17] which we later call paper I, we proposed a Monte Carlo technique to compute directly the *free-energy* difference $F_{N+1} - F_N$ between two clusters containing, respectively, $N+1$ and N particles. This energy difference is indeed the crucial parameter of the nucleation theory. A very similar technique (although less precise, cf. Sec. II) was proposed independently in Ref. 18.

In paper I the technique was assessed on the square Ising model for which the thermodynamical functions relevant to this study are known accurately. The technique consists of expressing the free-energy difference of interest as a thermal average which can be computed with high accuracy by Monte Carlo techniques.[19–23]

The main results of paper I are as follows:

(i) For the planar square Ising model with nearest-neighbor interactions, the cluster free-energy differences $F_{N+1} - F_N$ could be computed with an accuracy better than 2.5% within reasonable times for sizes up to 45 particles per cluster, and temperature ranging from 0.4 to 0.8 times the critical temperature.

(ii) The high accuracy thus obtained together with the availability of safe theoretical values for the thermodynamical functions of the bulk phases in the planar square Ising model allowed for discrimination between controversial expression of F_N. Our results are fully consistent with the following expression of the clusters' free energy F_N: ($N \geq 10$),

$$F_N=\tilde{N}\mu+\tilde{N}^{1/2}\Sigma+\beta^{-1}\tau\ln\tilde{N}+\tilde{d}\ , \qquad (1)$$

where $\tilde{N}=N/C_{\text{coex}}$, C_{coex} is the particles concentration in the dense bulk phase along the coexistence line between the dense and the dilute phases.

Equation (1) gives a good representation of the data down to surprisingly small sizes ($N \gtrsim 10$) provided that, β being the inverse temperature ($1/k_B T$), μ is given the value of the chemical potential of the particles at the coexistence line, Σ is given the value of the specific surface energy of a macroscopic drop having the *equilibrium shape*,[24,25] τ is given the recently proposed value: $\tau=1.25$,[26,27] and $\tilde{d}$ is a positive constant which is found to be temperature dependent and which can be interpreted as a curvature dependence of the surface specific energy.

In other words, the results of paper I are fully consistent with the capillarity description of a cluster provided that the surface-energy term is computed for the equilibrium shape and the curvature dependence of the surface energy is taken into account.

In the present paper we apply the technique of paper I to the three-dimensional simple cubic Ising model. Very-high-accuracy results are obtained which are very well fitted by an expression of the form

$$F_N=\tilde{N}\mu+\tilde{N}^{2/3}\Sigma+\tilde{N}^{1/3}\Lambda+\beta^{-1}\tau\ln\tilde{N}+\tilde{d}\ , \qquad (2)$$

where μ and τ are given their theoretical values.

The technique is briefly recalled in Sec. II while the data are described and discussed in Sec. III. Alternative expressions to Eq. (2) are discussed in Sec. IV and predictable consequences for the theory of nucleation are briefly discussed in Sec. V.

II. COMPUTATIONAL TECHNIQUE

The technique has been described in paper I (Secs. II and III). The computation starts with a cluster of N atoms B embedded in A atoms on a simple cubic lattice: A cubic box of M lattice sites with periodic boundary conditions is used. The condition $M>(N+1)^3$ ensures that the cluster is free to propagate without reaching unphysical configurations. Metropolis's algorithm is used for determining the probability of exchanging a randomly chosen A-B pair. Since A and B are not restricted to be nearest-neighbor atoms, a very efficient exploration of the configuration space is obtained.

For every configuration thus generated, we compute the fraction of B atoms which are linked by one bond to the cluster (f_N^-), and the ratio of the number of A atoms linked to the cluster by a simple bond to the total number of A atoms linked to the cluster (f_N^+). As explained in paper I, one finds after solving the computation for two cells containing N and $N+1$ B atoms, respectively,

$$\exp-\beta(F_{N+1}-F_N)=\frac{M-N}{N+1}\,\frac{f_N^+\exp(-\beta\Delta)}{f_{N+1}^-}\ , \qquad (3)$$

where Δ has the following form as a function of the pair interaction energies ($\epsilon_{AA},\epsilon_{AB},\epsilon_{BB}$):

$$\Delta=W_{AB}-Z(\epsilon_{AB}-\epsilon_{AA}) \qquad (4)$$

with $W_{AB}=2\epsilon_{AB}-\epsilon_{AA}-\epsilon_{BB}$ and Z is the coordination of the lattice ($Z=6$).

The results presented here were obtained using $\epsilon_{BB}=\epsilon_{AA}=0$, without loss of generality. We consistently used 10^5 Monte Carlo steps per B particle which yielded for $F_{N+1}-F_N$ an accuracy always better than $\pm 0.5\%$ within CPU (central processing unit) times of the order of 16 min for $N=20$ on a CDC 7600 computer.

For the interested reader, let us quote that we solved some computations using a biased sampling technique[28] aimed at reducing the variance of $f_N^{\pm}$. For the range of parameter values studied, no significant saving of computer time could be achieved. This conclusion may, however, not hold closer to the critical temperature.

The technique used in Ref. 18 is very similar although $F_{N+1}-F_N$ is found from a one-sided estimate, i.e., performing the exploration of the configuration space of one system (N particles) instead of two (N and $N+1$ particles). This simplified technique gave systematic deviation to the more precise estimation from Eq. (3), at least in the sytem we studied.

Finally, a still better estimate than that provided by Eqs. (3) and (4) can be obtained if we do not restrict to one the number of bonds broken or created by removing or adding a B atom to the cluster. Our data showed that the gain in precision thus obtained was not worth the increase in CPU time.[17–20]

III. NUMERICAL RESULTS: MODELING THE CLUSTER FREE ENERGY

Detailed data with an accuracy better than 0.5% have been obtained at two reduced temperatures ($T/T_c=0.4$ and 0.59) for sizes going from 1 to 20. Some data were also obtained at $T/T_c=0.8$ and for other crystal structures (fcc and bcc). These latter data are, however, not sufficiently complete to deserve a detailed discussion here.

Table I reproduces the data. In the second column $F_{N+1}-F_N$ is given in W_{AB} units.

Figures 1(a) and 1(b) represent the data of Table I. When compared to the two-dimensional case[17] the curves of Fig. 1 appear to be much more smooth at small sizes in three dimensions than in two dimensions. It seems that in three dimensions the noncompact configrations of a cluster of given N are relatively more degenerate than in two dimensions (contribution of nonplanar shapes); this results in a smoothening of the jumps in $F_{N+1}-F_N$ which corresponds to those N which allow for compact structures.

In view of the success of the capillarity model in describing the results in two dimensions (paper I) we first tried to describe the data of Figs. 1(a) and 1(b) by the following expression:

$$\frac{F_{N+1}-F_N}{W_{AB}}=a+b\,[(N+1)^{2/3}-(N)^{2/3}]+(\beta W_{AB})^{-1}\tau\ln\frac{N+1}{N} \qquad (5)$$

with, following the notation of paper I:

TABLE I. $F_{N+1}-F_N$ in units of the ordering energy (W_{AB}) as measured by the Monte Carlo technique, and deviation between experiment and simple capillarity [Eq. (5)] or complete expression [Eq. (8)], for two reduced temperatures. (a): $T/T_c=0.4$; (b): $T/T_c=0.59$. Note that the results for $N=1$ and 2 are exact.

	$(F_{N+1}-F_N)/W_{AB}$	$[(F_{N+1}-F_N)^{\rm theor}-(F_{N+1}-F_N)^{\rm expt}]/W_{AB}$	
N	measured	Eq. (5)	Eq. (8)
		(a)	
1	1.5045±0.0000	0.0344	−0.1579
2	1.2741±0.0000	0.0254	−0.0877
3	1.0997±0.0020	0.0638	−0.0134
4	1.0410±0.0014	0.0305	−0.0259
5	0.9744±0.0014	0.0287	−0.0139
6	0.9311±0.0021	0.0183	−0.0145
7	0.8784±0.0030	0.0274	0.0018
8	0.8542±0.0030	0.0150	−0.0049
9	0.8211±0.0029	0.0168	0.0014
10	0.8005±0.0029	0.0102	−0.0015
11	0.7744±0.0029	0.0123	0.0037
12	0.7632±0.0030	0.0021	−0.0039
13	0.7402±0.0031	0.0059	0.0021
14	0.7248±0.0031	0.0039	0.0020
15	0.7146±0.0030	−0.0018	−0.0020
16	0.6977±0.0030	0.0005	0.0017
17	0.6832±0.0030	0.0016	0.0041
18	0.6800±0.0032	−0.0077	−0.0040
19	0.6639±0.0033	−0.0033	0.0015
		(b)	
1	1.2691±0.0000	−0.3267	−0.5205
2	0.9292±0.0000	−0.1271	−0.2394
3	0.7611±0.0017	−0.0406	−0.1160
4	0.6807±0.0017	−0.0161	−0.0701
5	0.6215±0.0017	0.0013	−0.0387
6	0.5836±0.0017	0.0062	−0.0238
7	0.5542±0.0018	0.0087	−0.0139
8	0.5293±0.0020	0.0110	−0.0059
9	0.5123±0.0022	0.0086	−0.0037
10	0.4962±0.0021	0.0078	−0.0008
11	0.4805±0.0021	0.0086	0.0032
12	0.4714±0.0021	0.0044	0.0015
13	0.4658±0.0021	−0.0020	−0.0026
14	0.4490±0.0022	0.0039	0.0053
15	0.4405±0.0024	0.0024	0.0054
16	0.4389±0.0022	−0.0051	−0.0006
17	0.4327±0.0023	−0.0073	−0.0016
18	0.4238±0.0023	−0.0062	0.0007
19	0.4204±0.0023	−0.0100	−0.0021

$$a=\left[\frac{\mu_{\rm coex}}{W_{AB}}\right]C_{\rm coex}^{-1}\,, \tag{6}$$

where $\mu_{\rm coex}$ and $C_{\rm coex}$ are the B chemical potential and concentration along the coexistence line as given by the low-temperature expansions,[29]

$$b=(\Sigma/W_{AB})C_{\rm coex}^{-2/3}\,, \tag{7}$$

where Σ is the specific surface energy for the equilibrium shape of a drop in the simple cubic lattice. This quantity is not known. However, the (100) specific surface energy has been computed using the low-temperature expansion[30] and two estimates of b have been deduced assuming the equilibrium shape to be either spherical (b_s) or cuboidal (b_c). The corresponding values of b are given in Table II. τ has been given its recent theoretical value $\tau=-\frac{1}{9}$,[26] although Fisher's value ($\tau=2.2$) has also been tried and will be discussed later.[31]

Equation (5) was fitted to the data, leaving b as the only free parameter. The results are given in Table II. The b value obtained is in the range of the two estimates b_s and b_c. However, careful inspection of Fig. 1 and Table I re-

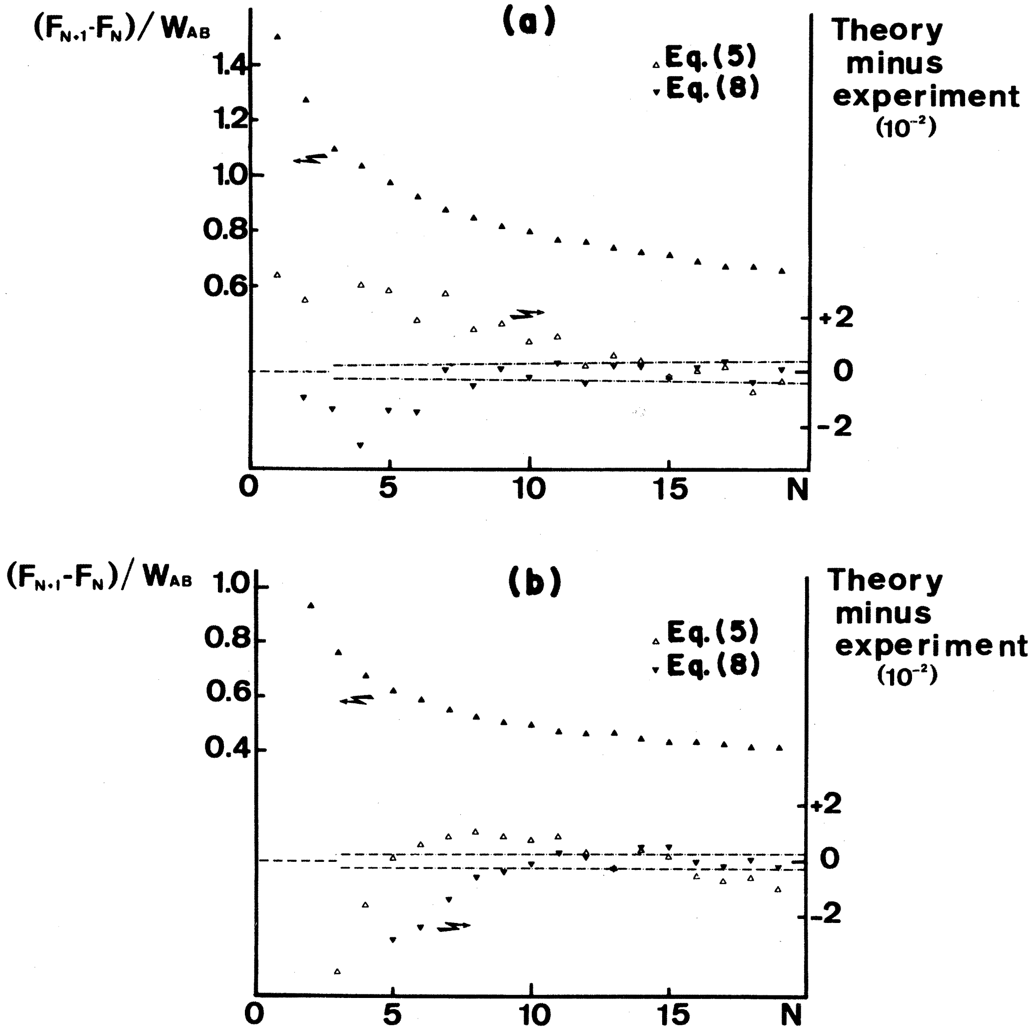

FIG. 1. Free-energy difference $(F_{N+1}-F_N)$ in W_{AB} units as a function of N, and theoretical minus experimental values for two fits [Eq. (5)] and [Eq. (8)]. (a) $T/T_c=0.4$; (b): $T/T_c=0.59$.

veals a *systematic deviation* between the data and Eq. (5), at small sizes (which is not surprising), but also at the larger sizes which is not acceptable in the spirit of the capillarity approximation. A better fit to the data is achieved by adding a $N^{1/3}$ term to the development of Eq. (5),

$$(F_{N+1}-F_N)/W_{AB}=a+b[(N+1)^{2/3}-N^{2/3}]$$
$$+c[(N+1)^{1/3}-N^{1/3}]$$
$$+(\beta W_{AB})^{-1}\tau\ln\frac{N+1}{N}\ . \quad (8)$$

Keeping the values of a and τ as before, the data have been fitted to Eq. (8) leaving b and c as free parameters. The results are given in Table II. The value of b is still in the range of the estimates b_s and b_c; the c term is *negative* and weakly temperature dependent. As seen in Fig. 1 and Table I, the introduction of the $N^{1/3}$ contribution to F_N eliminates the systematic deviation at larger sizes.

The $N^{1/3}$ contribution may be viewed as resulting from a curvature dependence of the surface free energy. Indeed, since curvature goes as $N^{-1/3}$, setting Σ_N instead of Σ in

TABLE II. Parameter values.

T/T_c	0.400	0.590
$\beta W_{AB}=2\beta\epsilon_{AB}$ [a]	2.2170	1.5030
$\mu^{\mathrm{coex}}/W_{AB}$ (Ref. 29)	−0.000 602	−0.008 33
C^{coex} (Ref. 29)	0.9986	0.985
a [Eq. (6)]	−0.000 603	−0.008 45
σ_{100}/W_{AB} (Ref. 30)	0.4873	0.3840
b_s	2.3587	1.8758
b_c	2.9264	2.3273
b measured [Eq. (5)]	2.680±0.016	1.7060±0.0081
b measured [Eq. (8)]	2.9461±0.0025	1.9964±0.0018
c measured [Eq. (8)]	−1.340±0.012	−1.4001±0.0089
$\beta^{-1}\tau/W_{AB}$	−0.0501	−0.0739
d measured [Eq. (5)]	0.0312±0.0048	1.7588±0.0041
d measured [Eq. (8)]	1.7129±0.0044	3.4416±0.0020

[a] In this calculation $\epsilon_{AA}=\epsilon_{BB}=0$.

Eq. (7) with

$$\Sigma_N=\Sigma_\infty(1+\epsilon N^{-1/3}) \tag{9}$$

yields Eq. (8) with

$$c=(\epsilon\Sigma_\infty/W_{AB})C_{\text{coex}}^{-1/3} . \tag{10}$$

The necessity of introducing a curvature dependence of ϵ was already found in two dimensions [d term in Eq. (1)]. Here c is found to be negative, in agreement with phenomenological models.[32,33] Note the correspondence between the notation of Eq. (9) and Tolman's notation,[32]

$$\epsilon=-\delta N^{1/3}/R ,$$

where R and δ are, respectively, the radius of the surface of tensions and the difference between the former radius and that of the surface of zero excess density.[32]

The fitting procedure may be pursued as follows. Since the values of $F_{N+1}-F_N$ have been computed for every single value of N, starting from 1, F_N can be found by summation,

$$F_N=\sum_{i=1}^{N-1}(F_{i+1}-F_i)+F_1 . \tag{11}$$

Note that F_1 is known exactly ($F_1=Z\epsilon_{AB}$). The results are given in Table III. As can be seen, even for the largest N available, the computed relative precision is still found to be smaller than 1%. Similarly, a theoretical expression F_N^{theor} of F_N can be obtained by summation of Eq. (8), yielding

$$\frac{F_N^{\text{theor}}}{W_{AB}}=aN+bN^{2/3}+cN^{1/3}+(\beta W_{AB})^{-1}\tau\ln\frac{N}{C_{\text{coex}}}+d , \tag{12}$$

where d is an integration constant which can be numerically determined as follows. From Eqs. (11) and (12) one obtains

$$F_N^{\text{expt}}-F_N^{\text{theor}}=F_1^{\text{expt}}-F_1^{\text{theor}}+\sum_{i=1}^{N-1}[(F_{i+1}-F_i)^{\text{expt}}-(F_{i+1}-F_i)^{\text{theor}}] , \tag{13}$$

where the superscript expt refers to the Monte Carlo results and where according to Eq. (12)

$$F_1^{\text{theor}}=a+b+c-(\beta W_{AB})^{-1}\tau\ln C_{\text{coex}}+d . \tag{14}$$

Since the parameter values in Eq. (8) were chosen in a way to eliminate the sytematic deviation between theory and experiment for $F_{N+1}-F_N$ at large N, the summation on the right-hand side of Eq. (13) yields for large values of N a quantity which fluctuates around a constant value which we note as

$$\left\langle\sum_{i=1}^{N-1}[(F_{i+1}-F_i)^{\text{expt}}-(F_{i+1}-F_i)^{\text{theor}}]\right\rangle .$$

The following choice of the integration constant d ensures that for large N, $F_N^{\text{expt}}-F_N^{\text{theor}}$ fluctuates around 0 as it should:

$$d=\frac{F_1^{\text{expt}}}{W_{AB}}-(a+b+c-\tau\ln C_{\text{coex}})+\left\langle\sum_{i=1}^{N-1}[(F_{i+1}-F_i)^{\text{expt}}-(F_{i+1}-F_i)^{\text{theor}}]\right\rangle . \tag{15}$$

As seen in Table II, the values of d thus determined are positive, temperature dependent, and contribute significantly to the free energy of the cluster (Table III).

As a final check we tried the value $\tau=2.2$ (Fischer, Ref. 31) following the above procedure. A systematic deviation between experimental values and values predicted from Eq. (8) appears for the large clusters. The same is true for the empirical value ($\tau=2.09$) proposed by Marro and Toral.[34]

Our data therefore support Eq. (12) which contains two new contributions as compared to the classical capillarity picture. Indeed, in addition to the bulk term (N), the surface term ($N^{2/3}$), and the logarithmic term, Eq. (12) contains a *"line" term* ($N^{1/3}$) and a *point term* (N^0).

One is tempted to relate the $N^{1/3}$ term to an edge energy and the N^0 term to a vertex energy. Indeed, the resistance of surface to bending in the Ising-square model was already phrased in terms of a corner energy,[35] and the existence of line contribution to the free energy of small clusters has been predicted in the case of a fluid lens embedded in two fluid phases.[36]

Physically, the line term produces the curvature dependence of the surface free energy. The point term might correspond to the bending of surface steps due to surface curvature in a direction perpendicular to the steps. This would be a jog energy.

The weight of each contribution to the cluster free energy is displayed in Table III. The cluster free energy is dominated by the surface contribution which is corrected by two major terms of opposite signs: the negative line contribution and the positive point contribution. The logarithmic term is very small. For the largest cluster size studied, the point contribution is roughly $-\frac{1}{2}$ the line contribution which is $-\frac{1}{5}$ the surface contribution, at low temperature. At higher temperaure ($0.59T_c$), the above figures become -1 and $-\frac{1}{4}$, respectively.

Before ending this section let us cite the results of Table IV. The computational algorithm we use gives as a byproduct the average internal energy E_N of the clusters (Table IV). In paper I ($F_{N+1}-F_N$) could not be computed for every single value of N up to the largest size, so that the knowledge of the E_N made useful information available. In the present study, fitting the internal energy gives no further understanding of the problem. Table IV simply makes the data available to the interested reader.

TABLE III. Free energy of the clusters (in W_{AB} units), as obtained by summation of the second column, of Table II [Eq. (11)] and contribution of each term of Eq. (12) to the measured value. (a) $T/T_c=0.4$; (b) $T/T_c=0.59$.

N	$\frac{F_N}{W_{AB}}$	aN	$bN^{2/3}$	$cN^{1/3}$	$\frac{1}{\beta W_{AB}}\tau\ln\left[\frac{N}{C^{\text{coex}}}\right]$	d
(a)						
1	3.0000±0.0000	−0.0006	2.9500	−1.3500	−0.0001	1.7129
2	4.5045±0.0000	−0.0012	4.6828	−1.7009	−0.0348	1.7129
3	5.7785±0.0000	−0.0018	6.1362	−1.9470	−0.0551	1.7129
4	6.8783±0.0020	−0.0024	7.4335	−2.1430	−0.0696	1.7129
5	7.9192±0.0024	−0.0030	8.6258	−2.3085	−0.0807	1.7129
6	8.8936±0.0028	−0.0036	9.7407	−2.4531	−0.0899	1.7129
7	9.8247±0.0035	−0.0042	10.7949	−2.5825	−0.0976	1.7129
8	10.7031±0.0046	−0.0048	11.8000	−2.7000	−0.1043	1.7219
9	11.5573±0.0055	−0.0054	12.7639	−2.8081	−0.1102	1.7129
10	12.3784±0.0062	−0.0060	13.6927	−2.9085	−0.1155	1.7129
11	13.1789±0.0069	−0.0066	14.5910	−3.0024	−0.1203	1.7129
12	13.9533±0.0074	−0.0072	15.4624	−3.0907	−0.1246	1.7129
13	14.7165±0.0080	−0.0078	16.3100	−3.1743	−0.1286	1.7129
14	15.4566±0.0086	−0.0084	17.1359	−3.2537	−0.1323	1.7129
15	16.1815±0.0091	−0.0090	17.9425	−3.3294	−0.1358	1.7129
16	16.8961±0.0096	−0.0096	18.7313	−3.4018	−0.1390	1.7129
17	17.594±0.010	−0.0102	19.5039	−3.4712	−0.1421	1.7129
18	18.277±0.010	−0.0108	20.2614	−3.5380	−0.1449	1.7129
19	18.957±0.011	−0.0115	21.0051	−3.6023	−0.1476	1.7129
20	19.621±0.011	−0.0121	21.7358	−3.6645	−0.1502	1.7129
(b)						
1	3.0000±0.0000	−0.0085	2.0000	−1.4100	−0.0011	3.4416
2	4.2691±0.0000	−0.0169	3.1748	−1.7765	−0.0524	3.4416
3	5.1983±0.0000	−0.0254	4.1602	−2.0336	−0.0823	3.4416
4	5.9594±0.0017	−0.0338	5.0397	−2.2382	−0.1036	3.4416
5	6.6400±0.0024	−0.0423	5.8480	−2.4111	−0.1201	3.4416
6	7.2615±0.0029	−0.0507	6.6039	−2.5621	−0.1336	3.4416
7	7.8452±0.0033	−0.0592	7.3186	−2.6972	−0.1450	3.4416
8	8.3994±0.0038	−0.0676	8.0000	−2.8200	−0.1548	3.4416
9	8.9287±0.0043	−0.0761	8.6535	−2.9329	−0.1636	3.4416
10	9.4410±0.0048	−0.0845	9.2832	−3.0378	−0.1713	3.4416
11	9.9372±0.0052	−0.0930	9.8922	−3.1358	−0.1784	3.4416
12	10.4177±0.0056	−0.1014	10.4830	−3.2281	−0.1848	3.4416
13	10.8890±0.0060	−0.1099	11.0576	−3.3154	−0.1907	3.4416
14	11.3549±0.0064	−0.1183	11.6176	−3.3983	−0.1962	3.4416
15	11.8038±0.0068	−0.1268	12.1644	−3.4774	−0.2013	3.4416
16	12.2444±0.0072	−0.1352	12.6992	−3.5530	−0.2061	3.4416
17	12.6833±0.0075	−0.1437	13.2230	−3.6255	−0.2106	3.4416
18	13.1160±0.0078	−0.1521	13.7366	−3.6953	−0.2148	3.4416
19	13.5398±0.0082	−0.1606	14.2407	−3.7625	−0.2188	3.4416
20	13.9602±0.0085	−0.1690	14.7361	−3.8273	−0.2226	3.4416

IV. OTHER EXPRESSIONS OF THE CLUSTER FREE ENERGY

The cluster free energy is often written in the form

$$\frac{F_N}{W_{AB}}=aN+bN^{\sigma}+\left[k_BT\frac{\tau}{W_{AB}}\right]\ln\left[\frac{N}{c_{\text{coex}}}\right]. \quad (16)$$

As discussed by Fisher,[31] the exponent σ should not be identical to the macroscopic value [$(D-1)/D$ where D is the dimensionality] for two reasons: the larger number of available configurations for larger clusters would increase σ, while cluster interference effects in the cluster gas at finite density would decrease σ. According to scaling arguments, Fisher concludes that $\sigma=1/\beta\delta$ (where now β is the critical exponent for the spontaneous magnetization and δ is that for the critical isotherm) or $\sigma=0.62\pm0.03$ for small clusters in three dimensions.

A Monte Carlo study of the surface area of droplets in the Ising model[37] supports a different expression for the surface term in Eq. (16): The surface area would vary as

TABLE IV. Measured average internal energy.

N	$T/T_c=0.400$ U^N/W_{AB} measured	$T/T_c=0.590$ U^N/W_{AB} measured
1	3.0000±0.0000	3.0000±0.0000
2	5.0000±0.0000	5.0000±0.0000
3	7.0000±0.0000	7.0001±0.0000
4	8.7528±0.0032	8.8617±0.0033
5	10.5232±0.0045	10.6941±0.0031
6	12.1637±0.0090	12.4632±0.0067
7	13.727±0.013	14.2051±0.0067
8	15.117±0.013	15.9091±0.0073
9	16.519±0.018	17.566±0.010
10	17.882±0.023	19.207±0.010
11	19.103±0.023	20.812±0.013
12	20.283±0.027	22.409±0.013
13	21.525±0.034	23.989±0.013
14	22.637±0.032	25.576±0.013
15	23.793±0.036	27.039±0.013
16	24.914±0.039	28.555±0.033
17	25.953±0.036	30.064±0.033
18	26.940±0.041	31.529±0.033
19	28.073±0.041	32.954±0.033
20	28.998±0.045	34.405±0.033

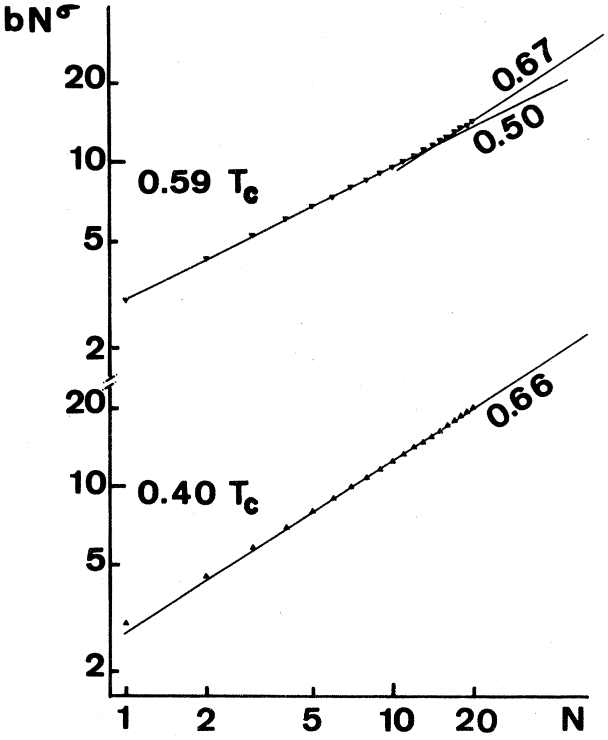

FIG. 2. Fit of F_N to Fisher's droplet model [Eq. (16)]. The ordinate is bN^σ in Eq. (16); σ values are given along the fitted lines. (a): $T/T_c=0.4$; (b): $T/T_c=0.59$. Dashed-dotted lines represent the experimental uncertainty.

$N\sigma'$ with $\sigma'=(1+\beta)/\beta\delta$ while the surface specific energy would vary as $N^{-1/\delta}$, at least for small clusters; for larger clusters, the macroscopic behavior is recovered with $\sigma'=(D-1)/D$. The cluster size where the transition occurs is temperature dependent, and scales with the correlation length to the third power. We tried to fit our data using Eq. (16) in the following way: Giving a and τ their theoretical value as discussed in the preceding section, we construct a log-log plot of

$$\frac{F_N^{\rm expt}}{W_{AB}}-\left[aN+\beta\tau\ln\frac{N}{C_{\rm coex}}\right]$$

vs N (Fig. 2). As can be seen, the plot is curved, the transition size being at $N^t \simeq 5$ at low temperature ($0.4T_c$) and $N^t \simeq 11$ at high temperature ($0.59T_c$). For the larger clusters ($N>N^t$), $\sigma=0.66$ fits well the low-temperature data, and it is not inconsistent with the high-temperature data (for $N=11$ to 19, we find $\sigma=0.6$ with a systematic deviation pointing to an upward curvature of the plot). For the smaller clusters ($N<N^t$) we cannot determine σ at low temperature because N^t is too small, while at high temperature $\sigma=0.5$ is consistent with the data. As seen in Fig. 2, $\sigma=1/\beta\delta=0.62$ is not consistent with the data at $0.59T_c$.

It should be stressed that the σ value thus determined is a property of the isolated cluster, while scaling arguments leading to $\sigma=1/\beta\delta$ apply to the macroscopic phase viewed as a gas of clusters. Cluster interference effects (excluded volume interaction) which contribute to the bulk properties have been shown to act as an effective surface-energy term.[38] The data presented here should help in assessing this latter term. Finally the transition size N^t varies with the temperature and scales well with the third power of the correlation length extrapolated from the critical temperature.[37]

As a last check, we compare our data at $0.59T_c$ to the values predicted by Penrose and co-workers[39,40] following an empirical fit to computer simulation data:[41]

$$\beta(F_{N+1}-F_N)=\alpha\ln\left[W_s\left[1+\frac{C}{(N+2)^{1/3}}\right]\right] \tag{17}$$

with $\alpha=1$, $W_s=0.010\,526$, and $C=2.415$ at $0.59T_c$. Figure 3 depicts our data plotted as a function of $\ln[W_s(1+C/(N-2)^{1/3}]$. As can be seen in Fig. 3, the values of Penrose and Buhagiar[40] underestimate $F_{N+1}-F_N$ for larger cluster sizes.

When fitted to a straight line, our data yield for $4\leq N\leq 19$

$$\alpha=0.959,\quad W_s=0.02873$$

or for $9\leq N\leq 19$

$$\alpha=0.880,\quad W_s=0.01154\ .$$

Alternatively, Eq. (17) may be fitted to our data, leaving $\alpha=1$ and keeping W_s and C as adjustable parameters; for $4\leq N\leq 19$ we get

$$W_s=0.011\,15\pm0.000\,08,\quad C=2.216\pm0.031.$$

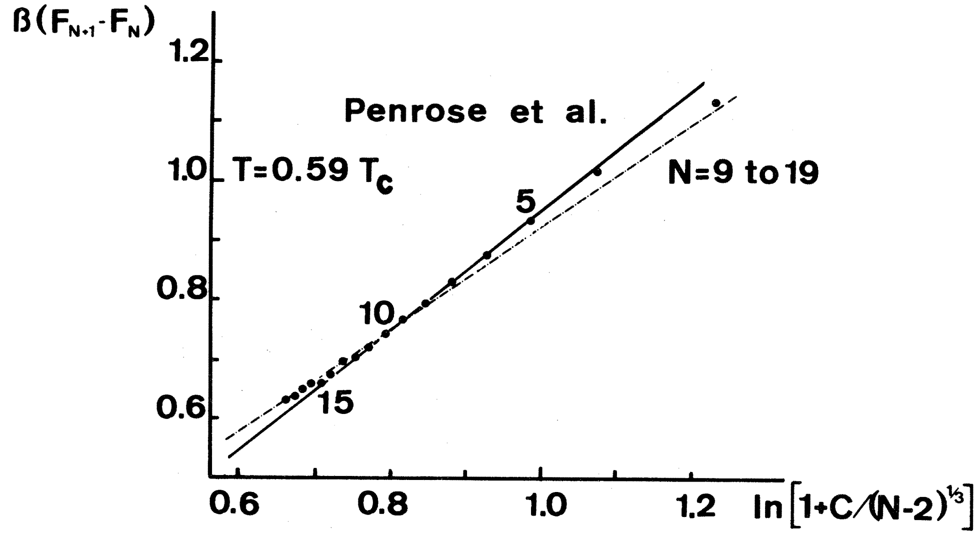

FIG. 3. Fit of $(F_{N+1}-F_N)$ to the model of Penrose *et al.* [Eq. (17)] at $T/T_c=0.59$. Note that we use $\epsilon_{AA}=\epsilon_{BB}=0$ while Ref. 40 uses $\epsilon_{AA}=\epsilon_{AB}=0$. For the same reduced temperature, the values of $\beta(F_{N+1}-F_N)$ reported here are shifted up by $6\beta\epsilon_{AB}$ $(=4.5089)$ with respect to Ref. 40. The labels 5, 10, and 15 give the value of N for the corresponding points. The dashed line was fitted to points $9\le N\le 19$.

V. CONSEQUENCES FOR THE NUCLEATION THEORY

The data presented here can be used to assess the various simplifying assumptions which are the basis of the classical nucleation theory of unmixing. Indeed, the kinetics of unmixing in the simple cubic Ising model has been well studied using Monte Carlo techniques.[39,41,42–48] The data presented here are currently being used as ingredients of the nucleation theory: The results will be compared to the data obtained on the kinetic Ising model. These results will be published elsewhere.

A rough estimate of typical effects of the line and point contributions to the cluster energy [Eq. (12)] on the nucleation rate can be found as follows. The stationary nucleation rate J_s is proportional to the concentration of critical nuclei N^* defined by

$$\left.\frac{\partial F_N}{\partial N}\right|_{N=N^*}=0 . \tag{18}$$

Therefore, as a first approximation,

$$J_s \propto \exp(-\beta F_N^*) . \tag{19}$$

We compare the estimates of J_s given by alternative expressions of F_N, for a given supersaturation [i.e., for a given negative value of a in expression (12)]. The expressions of F_N are Eqs. (12) on the one band and a capillarity expression obtained by setting $c=d=0$ in Eq. (12) and giving b either the value obtained by the fit of the data with Eq. (5) (cf. Table II), or the estimated values for a spherical or a cuboidal critical nucleus. For the sake of completeness, $\tau=0$ is also studied. The computation is done at two temperatures (0.4 and $0.59T_c$) with two supersaturations yielding to correct critical sizes either small $(N^*\simeq 5)$ or large $(N^*\simeq 19)$.

Taking as a reference the value of J_s as obtained using the best expression for F_N [Eq. (12)], all capillaritylike expressions of F_N give nucleation rates within a factor of 10^2-10^{-3} of the reference rate. The cuboidal shape approximation for the critical nucleus always results in an underestimation of the nucleation rate (by a factor up to 10^3). All other approximations overestimate the nucleation rate by a factor smaller than 10^2. Therefore, naive capillarity descriptions of the critical nucleus leave a range of uncertainty of 5 orders of magnitude on the true nucleation rate. The highest sensitivity of the nucleation rate to the choice of the expression of F_N is of course obtained at lower supersaturations, but also at higher temperature. This results from the temperature variation of the surface specific energy.

The above conclusions cannot be simply compared to the existing predictions of the effect of the curvature dependence of the surface energy on the nucleation rate.[8] Using our experimental values, we get in Heermann's notations $0.4\le y\le 0.6$ which would imply a lowering of the critical radius when the curvature correction is taken into account. Such is not the general case for the following reason: for the cluster sizes studied, the surface-energy contribution obtained by fitting the data (b in Table II) is not the same whether the curvature correction is included [Eq. (8)] or not [Eq. (5)]. In other words Heermann's treatment assumes that the specific surface energy along the equilibrium shape is known, while in the present study it must be extracted from the data.

VI. CONCLUSION

Direct Monte Carlo computation of the free-energy difference between clusters comprising $N+1$ and N particles (solute atoms) following the technique of paper I (Ref. 17) has been done in the simple cubic Ising model for every value of N from 1 to 19 at 0.4 and 0.59, the critical temperature. The summation of the results from $N=1$ to $N-1$ yields the free energy F_N of the cluster with an accuracy better than 1%.

The free energy F_N (in units of the ordering energy W_{AB}) is best described by the expression:

$$\frac{F_N}{W_{AB}} = aN + bN^{2/3} + cN^{1/3} + d + \frac{\beta\tau^{-1}}{W_{AB}} \ln\frac{N}{C_{\text{coex}}} \,,$$

where a and τ are given their theoretical value, and b, c, and d represent, respectively, surface, line, and point contributions.

The line contribution corresponds to the curvature dependence of the surface free energy while the point contribution is tentatively ascribed to the cross curvature dependence of the surface steps energy. Other expressions of the clusters free energy (Fisher's droplet model[31] or empirical expressions[39]) deviate from our data.

A rough estimate of nucleation rates for unmixing in the model system under study shows that the various capillarity approximations of F_N yield nucleation rates ranging from 10^2 to 10^{-3} that predicted using the correct values of F_N, i.e., leaving an uncertainty of about 5 orders of magnitude on the nucleation rate.

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