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Monte Carlo computation of cluster free energies in the Ising model: a test for the validity of the capillarity approximation

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Abstract. A new Monte Carlo technique is proposed to compute directly the free energy difference $F_{N+1} - F_N$ of two clusters with size $N + 1$ and N . The algorithm is applied to the two-dimensional square Ising model with nearest-neighbour interactions. Results are given for $1 \leq N \leq 45$ at temperatures T ranging from 0.4 to 0.8 of the critical temperature. A very high accuracy (1 to 2%) is achieved within reasonable computer time. The results are compared to the prediction of the capillarity model ($F_N = N\mu + N^{1/2}\Sigma + (\tau/\beta) \ln N$) where the intensive variables (μ : chemical potential, Σ : specific surface energy for the equilibrium shape, $\beta = 1/kT$) are given their equilibrium value for bulk phases, known exactly for the two-dimensional square Ising model. An excellent agreement is achieved from sizes $N > 9$, yielding a value of τ very close to 1.25 as predicted by recent theories. For smaller cluster sizes, F_N is computed by direct summation of $F_{N+1} - F_N$. The obtained energies are larger than predicted by the capillarity model. The deviation exhibits no systematic size dependence, but a strong temperature dependence. The existence of a size independent term in F_N is confirmed by the values of the internal energy U_N obtained as a by-product of the calculation. This constant may be interpreted as a curvature dependence of the surface free energy: the larger the curvature, the larger the surface free energy.

Résumé. On propose une nouvelle technique de Monte Carlo pour calculer directement la différence des énergies libres $F_{N+1} - F_N$ de deux amas de taille $N + 1$ et N . L'algorithme est appliqué au modèle d'Ising carré, à deux dimensions, avec interaction entre premiers voisins. On donne des résultats pour $1 \leq N \leq 45$ à des températures allant de 0,4 à 0,8 la température critique. Des temps de calcul raisonnables permettent d'atteindre une très grande précision (1 à 2%). On compare les résultats aux prédictions du modèle capillaire ($F_N = N\mu + N^{1/2}\Sigma + \tau/\beta \ln N$ avec $\beta = 1/kT$) où on attribue aux paramètres (μ : potentiel chimique, Σ énergie spécifique de surface) leur valeur d'équilibre dans les phases massives, connues précisément pour le modèle d'Ising à deux dimensions. Pour les tailles $N > 9$, un accord excellent est obtenu, conduisant à une valeur de τ très voisine de 1,25 prédite par les théories récentes. Pour les amas plus petits, F_N est calculé par sommation directe de $F_{N+1} - F_N$. Les énergies obtenues sont supérieures à celles prévues par le modèle capillaire. L'écart est indépendant de la taille mais dépend fortement de la température. La présence d'un terme indépendant de la taille dans F_N est confirmée par les valeurs de l'énergie interne U_N obtenues comme sous produit du calcul. Cette constante peut être interprétée comme un effet de courbure sur l'énergie de surface: l'énergie libre de surface croît avec la courbure.

1. Introduction

The free energy F_N of a cluster of size N is the central quantity of nucleation theory (for a review see Binder and Stauffer 1976). The expression of F_N is still controversial. The classical theory of nucleation rests on the 'capillarity model', where F_N is the sum of a bulk term (aN) and a surface term ($bN^{(d-1)/d}$, $d = \text{dimensionality}$); the intensive variables of the model are given their bulk value. On the other hand, statistical mechanical treatments show that F_N should contain a logarithmic term $\tau\beta^{-1} \ln N$ (Fisher 1967) the coefficient of which has been recently re-evaluated (Wallace 1981); here $\beta^{-1} = \text{Boltzmann constant times the absolute temperature}$.

Moreover, the value of the exponent of N in the surface term is also under discussion (Fisher 1967, Binder and Stauffer 1972), with the possibility of a crossover from small N to macroscopic values when the droplet size is much larger than the correlation length.

Due to the inherent difficulty in measuring F_N experimentally in real systems, it has often been tried to compute F_N numerically for simple model systems such as the Lennard-Jones—or the lattice gas model—(for a review see Burton and Briant 1977). However, the degree of accuracy reached up to now has not been sufficient to allow for a clear discrimination among conflicting models. Such is the case, in particular for a recent simulation (Binder and Kalos 1980) of the two-dimensional lattice gas model at low temperature. The authors concluded that the inadequacy of the capillarity model accounted for their results; also the accuracy was not sufficient to reveal the necessity for the logarithmic correction. The same limitation occurred in a computer simulation of the Coniglio-Klein model (Rousseny 1982).

It therefore seemed useful to develop a high-accuracy computation technique for F_N , with the aim of discriminating between controversial theories when available, and of producing data in fields of interest where no theories are yet available.

Here we focus on the lattice gas model due to its simplicity and to the existence of rigorous expressions for the relevant thermodynamical functions in two dimensions (Onsager 1944). In this model, the only contribution to the cluster-free energy comes from the configurational partition function Q_N

$$F_N = -\beta^{-1} \ln Q_N \quad Q_N = \sum_i \exp(-\beta U(C_i^N)). \quad (1)$$

The sum extends to all configurations C_i^N of a cluster of N indistinguishable particles counting only one C_i^N out of each of translationally equivalent configurations. $U(C_i^N)$ is the potential energy associated with C_i^N . For the lattice gas model, the cluster is unambiguously defined as a set of occupied sites connected by nearest-neighbour bonds.

For small values of N , Q_N can be computed exactly by a systematic exploration of all the possible C_i^N . This technique fails for N larger than a few units. For larger N values, one should turn to machine calculations.

We present here a Monte Carlo technique for computing directly Q_{N+1}/Q_N and therefore $F_{N+1} - F_N$ from equation (1), with high accuracy. The use of the Monte Carlo method to calculate free energy differences is essentially a 'computer calorimetry' (Bennett 1976, Valleau and Torrie 1977). It has already been used successfully in various problems of solid state physics (Jacucci and Ronchetti 1980, Jacucci and Quirke 1982).

The method is applied to the two-dimensional square Ising model and to $N < 50$ although much larger clusters have been studied within reasonable computer times ($N < 100$). Three temperatures have been investigated ($T/T_c = 0.801, 0.588, 0.401$). As will be seen, the logarithmic term in F_N is well identified, the coefficient τ is in close agreement with the recent derivation (Wallace 1981, 1982, Lowe and Wallace 1980) $\tau = 1.25$. The remaining part of $F_{N+1} - F_N$ is well accounted for by the capillarity approximation provided that the anisotropy of the surface tension in the square Ising model is taken into account (Fisher and Ferdinand 1967, Abraham and Reed 1977): the specific surface energy of the cluster must be given the value computed for a droplet with the equilibrium shape (Avron *et al* 1982, Zia and Avron 1982). The capillarity model thus constructed well represents the results down to surprisingly small sizes ($N \approx 10$). Moreover, as will be seen, a size independent term is anticipated in F_N , the value of which is strongly temperature dependent. This term may be viewed as a curvature dependence of the surface specific energy.

In the following, we first present the computation technique, then the results together with their fit to the capillarity model, and finally discuss the implication of these results.

2. Computational method

We want to evaluate F_N as defined by equation (1). To be more specific, we deal with the binary alloy version of the Ising model, with nearest-neighbour interactions. We restrict ourselves to the two-dimensional simple square lattice.

The system is a lattice with M sites, each of which is occupied by an A or a B particle which interacts with its four nearest neighbours with interaction energies ϵ_{AA} , ϵ_{AB} , ϵ_{BB} . The configuration of the system is specified by giving the particle type on each site. The energy of each configuration can be written:

$$U = N_{AB} \frac{1}{2} W_{AB} + 2(N_A \epsilon_{AA} + N_B \epsilon_{BB}) \tag{2}$$

where N_{AB} is the number of AB bonds, N_A , N_B the number of A , respectively B particles and the ordering energy W_{AB} is given by

$$W_{AB} = 2\epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB}). \tag{3}$$

For the sake of simplicity we choose

$$\epsilon_{AA} = \epsilon_{BB} = 0. \tag{4}$$

The correspondence between the above model and notations with the classical Ising model is given in table 1 (cf appendix 1).

Since we are interested in the partition function of one cluster of N particles, we restrict the configurational space to those configurations for which each 'solute atom' B is linked to the cluster by at least one nearest-neighbour bond. This is achieved

Table 1. Correspondence between the Ising and the binary alloy metal. μ_α is the chemical potential of α .

	Ising	Alloy
Interaction energy	4J	W_{AB}
External field	mH	$\epsilon_{BB} - \epsilon_{AA} + (\mu_A - \mu_B)/2$

by artificially setting an infinite value to the Hamiltonian of the system if more than one cluster is present.

With the above correspondences, the free energy per particle for the bulk phase in zero field for the two systems is related by:

$$\mu_{\text{coex}} = \varepsilon_{AB} - (1/N\beta) \ln Q_N^{\text{Ising}}. \quad (5)$$

$\mu_{\text{coex}} (= \mu_A = \mu_B)$ is the common value of the chemical potential of A and B along the coexistence line.

A direct Monte Carlo computation of F_N is not feasible for the same general reasons which apply to any free energy calculation (Valleau and Torrie 1977). However, free energy differences can be accurately computed by recently developed methods based on energy distribution functions (Valleau and Torrie 1977, Bennett 1976, Jacucci and Ronchetti 1980, Jacucci and Quirke 1982). These methods consist in expressing the free energy difference of interest as a thermal average which can be accurately computed, provided that the statistical ensembles of the two systems overlap sufficiently. The method is outlined in appendix 2. It is shown that the free energy difference $F_{\text{II}} - F_{\text{I}}$ may be computed from

$$\exp -\beta(F_{\text{II}} - F_{\text{I}}) = Q_{\text{II}}/Q_{\text{I}} = (f_{\text{I}}(\Delta) \exp -\beta\Delta)/f_{\text{II}}(\Delta) \quad (6)$$

where $\Delta = U_{\text{II}} - U_{\text{I}}$ is the difference potential energy for each configuration under Hamiltonians II and I respectively,

$$\begin{aligned} f_{\alpha}(\Delta) &= \langle \delta(\Delta - U_{\text{II}} + U_{\text{I}}) \rangle_{\alpha} \\ &= Q_{\alpha}^{-1} \sum_i \delta(\Delta - \Delta(C_i)) \exp[-\beta U_{\alpha}(C_i)] \end{aligned} \quad (7)$$

where $\Delta(C_i)$ is the value of Δ in configuration C_i and \sum_i stands for the summation over all configurations C_i . $f_{\alpha}(\Delta)$ is the distribution of the energy differences between systems I and II. Equation (6) may be intuitively understood as follows: the distributions $f_{\alpha}(\Delta)$ give the fraction of configurations in each ensemble corresponding to a given value of Δ . In ensemble II, let i be a configuration which contributes to this fraction. Such a configuration appears with the weight $\exp(-\beta U_{\text{II}}^i)/Q_{\text{II}}$. Similarly, a configuration i in ensemble I which contributes to $f_{\text{I}}(\Delta)$ appears with the weight $\exp(-\beta U_{\text{I}}^i)/Q_{\text{I}}$. The ratio r of the above two statistical weights is a function of Δ , Q_{I} , Q_{II} only. It is therefore the same for all configurations which contribute to $f_{\text{II}}(\Delta)$ and $f_{\text{I}}(\Delta)$, and is written $r(\Delta) = \exp(-\beta\Delta)Q_{\text{I}}/Q_{\text{II}}$. The distributions $f_{\alpha}(\Delta)$ are just the sums of the weights in the respective ensembles, and their ratio will also coincide with $r(\Delta)$, yielding equation (7).

The Monte Carlo procedure simply follows from this remark. The distributions f_{I} and f_{II} are estimated by two independent Monte Carlo runs on ensembles I and II respectively. If the distributions thus obtained do overlap on some range Δ , $Q_{\text{II}}/Q_{\text{I}}$ can be estimated from equation (6).

A delicate question arises in applying this method to the calculation of the cluster free energy difference $F_{N+1} - F_N$. The system we study is made of a box of M lattice sites occupied by N (or $N+1$) B atoms and respectively $M-N$ (or $M-N-1$) A atoms. From each configuration of system (N) we want to build one configuration of system ($N+1$) so as to be able to define Δ . Similarly for building a configuration of system N from one configuration of system ($N+1$). In order to do this unambiguously,

we must use configurations of *distinguishable* particles. Simple combinatorial analysis shows that the ratio of the configurational partition functions for the boxes of M sites containing respectively N and $(N + 1)$ B particles and respectively $M - N$ and $M - (N + 1)$ A particles for both distinguishable and indistinguishable particles is

$$\frac{Q_{N+1}}{Q_N} = \frac{M - N}{N + 1} \frac{\hat{Q}_{N+1}}{\hat{Q}_N} \quad (8)$$

where the symbol $\hat{}$ indicates the system with distinguishable particles. It is worth mentioning that each class of translationally equivalent configurations of the system which defines a configuration of the cluster, contains M configurations so that Q_{N+1}/Q_N in equation (8) is the ratio of the partition functions of *clusters* with sizes $N + 1$ and N .

In conclusion, introducing the distribution functions $f_{N+1}(\Delta)$ and $f_N(\Delta)$ for *distinguishable* particle systems, we can write, according to equations (6) and (8):

$$\exp[-\beta(F_{N+1} - F_N)] = \frac{Q_{N+1}}{Q_N} = \frac{M - N}{N + 1} \frac{f_N(\Delta) \exp(-\beta\Delta)}{f_{N+1}(\Delta)}. \quad (9)$$

3. Technical remarks

In practice the computation starts with a compact cluster of N atoms B at the centre of a box of M lattice sites with periodic boundary conditions. The condition $M > (N + 1)^2$ ensures that the cluster is free to propagate without reaching unphysical configurations. One A atom and one B atom are chosen at random; A and B are exchanged with a probability given by Glauber's or Metropolis' algorithm (for a review see Kawasaki, 1972). Note that A and B need to be nearest-neighbour atoms, so that a very efficient exploration of the configuration space is performed. For each configuration thus generated, we compute on the one hand what the energy change would be if one A atom were turned into a B atom, and on the other hand what this energy change would be if one B atom were turned into an A atom. Obviously this energy change Δ may take five values ($\Delta/W_{AB} = 1, 2, 3, 4, \infty$) depending:

- (i) on the number of bonds connecting the site under consideration to B atoms and
- (ii) on the possibility that this operation destroys the cluster.

Efficiency is improved by performing the computation of Δ for each B and each A atom of each configuration of the Monte Carlo chain. The distributions $f_N(\Delta)$ and $f_{N+1}(\Delta)$ which enter equation (9) are estimated from the histograms of Δ values constructed according to the above procedure.

In principle, according to equation (9), five estimations $F_{N+1} - F_N$ are so produced, one for each value of Δ according to equation (9). The technique for finding the best estimate of $F_{N+1} - F_N$ together with its uncertainty has been described (Bennett 1976). However, for the sake of saving computer time, we only compute $f(\Delta)$ for $\Delta/W_{AB} = 1$: indeed on changing into an A , a B atom which is linked to the cluster by one bond only, surely conserves the cluster and no further check is needed. The number of Monte Carlo steps has been typically 250 000 per atom in the cluster; but due to various degeneracies of configurations, after the introduction of various optimisation procedures, the computer time has been found to increase with N as N^x with $x \approx 1.7$ and is typically of the order of 40 minutes on a CDC 7600 computer for a cluster of 45 atoms.

4. Numerical results and interpretation

Detailed high-accuracy calculations have been performed for βW_{AB} of 2.2, 3.0 and 4.4, corresponding to reduced temperatures (T/T_c) of respectively 0.801, 0.588, 0.401. The cluster sizes ranged from 1 to 45. For small sizes ($1 < N < 5$) Q_N was computed analytically, and checked numerically for $N = 4$ and $N = 5$. Results are given in tables 2 (a, b, c (first column)) where $F_{N+1} - F_N$ is expressed in W_{AB} units. As can be seen, the uncertainty is always smaller than 2.5%. The other columns of tables 2 allow for

Table 2. Measured values of $F_{N+1} - F_N$ and comparison with equations (14)–(15). (a), $T/T_c = 0.801$; $\beta W_{AB} = 2.2$; $a = -0.0074$, $b = 0.665$; $\tau/W_{AB} = 0.568$.

N	$(F_{N+1} - F_N)/W_{AB}$ Measured	$(\tau/W_{AB}) \ln \frac{N+1}{N}$	$(F_{N+1} - F_N)/W_{AB}$ Equations (14)–(15)
1	0.6849 ± 0.0000	0.3937	0.6618
2	0.5005 ± 0.0000	0.2303	0.4343
3	0.3186 ± 0.0007	0.1634	0.3342
4	0.2953 ± 0.0011	0.1267	0.2763
5	0.2260 ± 0.0016	0.1036	0.2381
6	0.2213 ± 0.0016	0.0876	0.2107
7	0.1856 ± 0.0016	0.0759	0.1899
8	0.1714 ± 0.0016	0.0669	0.1736
9	0.1562 ± 0.0015	0.0598	0.1604
15	0.1087 ± 0.0013	0.0367	0.1137
19	0.0919 ± 0.0015	0.0291	0.0970
25	0.0738 ± 0.0017	0.0223	0.0807
29	0.0727 ± 0.0015	0.0193	0.0731
35	0.0611 ± 0.0015	0.0160	0.0644
39	0.0533 ± 0.0014	0.0144	0.0599
45	0.0545 ± 0.0014	0.0125	0.0544

Table 2. Measured values of $F_{N+1} - F_N$ and comparison with equations (14)–(15). (b), $T/T_c = 0.588$; $\beta W_{AB} = 3$; $a = -0.0009$; $b = 1.250$, $\tau/W_{AB} = 0.417$.

N	$(F_{N+1} - F_N)/W_{AB}$ Measured	$(\tau/W_{AB}) \ln \frac{N+1}{N}$	$(F_{N+1} - F_N)/W_{AB}$ Equations (14)–(15)
1	0.7690 ± 0.0000	0.2890	0.8063
2	0.6338 ± 0.0000	0.1691	0.5658
3	0.3841 ± 0.0011	0.1200	0.4542
4	0.4236 ± 0.0008	0.0931	0.3874
5	0.2968 ± 0.0023	0.0760	0.3421
6	0.3436 ± 0.0023	0.0643	0.3089
7	0.2605 ± 0.0021	0.0557	0.2833
8	0.2659 ± 0.0021	0.0491	0.2628
9	0.2448 ± 0.0017	0.0439	0.2460
15	0.1822 ± 0.0016	0.0269	0.1849
19	0.1566 ± 0.0016	0.0214	0.1621
25	0.1404 ± 0.0017	0.0164	0.1393
29	0.1282 ± 0.0016	0.0141	0.1284
35	0.1169 ± 0.0016	0.0118	0.1158
39	0.1104 ± 0.0015	0.0106	0.1092
45	0.1028 ± 0.0017	0.0092	0.1010

Table 2. Measured values of $F_{N+1} - F_N$ and comparison with equations (14)–(15). (c), $T/T_c = 0.401$; $\beta W_{AB} = 4.4$; $a = -0.000035$; $b = 1.644$; $\tau/W_{AB} = 0.284$.

N	$(F_{N+1} - F_N)/W_{AB}$ Measured	$(\tau/W_{AB}) \ln \frac{N+1}{N}$	$(F_{N+1} - F_N)/W_{AB}$ Equations (14)–(15)
1	0.8425 ± 0.0000	0.1969	0.8782
2	0.7503 ± 0.0000	0.1152	0.6379
3	0.3620 ± 0.0017	0.0817	0.5224
4	0.5544 ± 0.0005	0.0634	0.4516
5	0.2791 ± 0.0036	0.0518	0.4028
6	0.4857 ± 0.0034	0.0438	0.3665
7	0.2583 ± 0.0032	0.0379	0.3383
8	0.3122 ± 0.0022	0.0335	0.3156
9	0.3402 ± 0.0018	0.0299	0.2968
15	0.2386 ± 0.0023	0.0183	0.2272
19	0.1992 ± 0.0023	0.0146	0.2008
25	0.1713 ± 0.0023	0.0111	0.1740
29	0.1579 ± 0.0025	0.0096	0.1610
35	0.1457 ± 0.0023	0.0080	0.1460
39	0.1367 ± 0.0025	0.0072	0.1380
45	0.1315 ± 0.0023	0.0062	0.1281

the comparison of the measured values with the prediction of the capillarity approximation.

For F_N we choose the expression

$$F_N = \tilde{N}\mu + \tilde{N}^{1/2}\Sigma + \beta^{-1}\tau \ln \tilde{N} \tag{10}$$

where \tilde{N} is the number of atoms (A and B) in the cluster, μ the chemical potential and Σ is the specific surface free energy of the cluster with the equilibrium shape. Indeed the B cluster equilibrates with A atoms by incorporating them in proper proportion (with the restriction that configurations which imply an inclusion of A atoms containing a B inclusion are avoided: such configurations are irrelevant for the small clusters at low temperature which are under study here). In equation (10),

$$\tilde{N} = N/C \tag{11}$$

where C is the B concentration in the cluster. In agreement with the classical capillarity approximation, we assume in the following:

$$\mu = \mu_{\text{coex}} \quad C = C_{\text{coex}} \tag{12}$$

where C_{coex} is the B concentration in the bulk B -rich phase, in equilibrium with the dilute phase. Expressions for μ_{coex} and C_{coex} are given in appendix 1.

As far as the surface term is concerned, it should be stressed that the capillarity approximation rests on the assumption that the cluster has a macroscopic equilibrium shape (for a review see Martin, 1975). Due to the anisotropy of the surface tension in the square Ising model (Fisher and Ferdinand 1967, Abraham and Reed 1977), the equilibrium shape is not circular. In the case of the solid-on-solid model, an approximate expression has been given for the equilibrium shape of a 2D cluster on a surface with a square lattice cell and first- or first- and second-nearest-neighbour interaction (Burton *et al* 1950–1951). More recently, an exact expression for the equilibrium shape of a macroscopic cluster in the two-dimensional square Ising model

has been derived (Zia and Avron 1982, Avron *et al* 1982). By numerical integration along the contour of this shape, it is possible to compute the surface specific free energy for the equilibrium shape (see equation (3) in Zia and Avron 1982). As expected, the equilibrium shape is a square at 0 K and a circle at the critical temperature. In between, it looks like a square with rounded corners, although the curvature is everywhere finite. The values of the surface specific free energy thus computed are reported in table 3.

Table 3. Theoretical values of useful parameters computed from the known solutions of the 2D Ising model. $\tau\beta/W_{AB}$ is computed for $\tau = 1.25$.

T/T_c	0.801	0.588	0.401
βW_{AB}	2.2	3.0	4.4
μ_{coex}/W_{AB}	-0.0072	-0.0009	-0.000035
C_{coex}	0.9784	0.9969	0.9998
a	-0.0074	-0.0009	-0.000035
Σ	0.658	1.249	1.645
$C_{\text{coex}}^{1/2}$	0.9891	0.9984	1.0
b	0.665	1.251	1.645
$\beta\tau/W_{AB}$	0.568	0.417	0.284

Finally, the value of τ which was initially predicted ($\tau = 2.067$, Fisher 1967) has been recently re-estimated as 1.25 (Wallace 1981, 1982, Lowe and Wallace 1980).

The capillarity approximation as expressed by equation (10) together with the above conventions for the ingredients of equation (10) may be compared to the row data of table 2 noticing that

$$\beta(F_{N+1} - F_N) = \beta \frac{\mu_{\text{coex}}}{C_{\text{coex}}} + \beta \frac{\Sigma}{\sqrt{C_{\text{coex}}}} (\sqrt{N+1} - \sqrt{N}) + \tau \ln \frac{N+1}{N} \quad (13)$$

or equivalently

$$(F_{N+1} - F_N)/W_{AB} = a + b(\sqrt{N+1} - \sqrt{N}) + (\beta W_{AB})^{-1} \tau \ln \frac{N+1}{N} \quad (14)$$

with:

$$a = (\mu_{\text{coex}}/W_{AB})C_{\text{coex}}^{-1} \quad b = (\Sigma/W_{AB})C_{\text{coex}}^{-1/2} \quad (15)$$

where Σ is the surface specific free energy. The values of a , b and $\tau(\beta W_{AB})^{-1}$ are given in table 3 for the relevant temperatures, assuming $\tau = 1.25$.

In tables 2 (a , b and c) the contribution of the last term of the RHS of equation (14) to the final result is shown, together with the raw data for the three reduced temperatures. Figure 1 shows the excellent agreement between the raw data and the values predicted from equations (14) and (15). As can be seen, the agreement is very good down to surprisingly small sizes ($N \sim 10$ or even smaller at higher temperatures). At the lower temperature, a large scatter of the raw data appears already from $N = 15$. This deterioration should be expected since at 0 K, F_N is a non-analytical function of N .

The second point to be noticed in table 2 is that the logarithmic term in equation (14) brings indeed an important contribution at the temperatures under consideration: at the lower temperature ($T/T_c = 0.401$) the logarithmic term contributes to $F_{N+1} - F_N$ by 4-8% for N equal to 45 and 15 respectively, while at higher temperatures ($T/T_c = 0.801$) this contribution ranges from 18 to 32%.

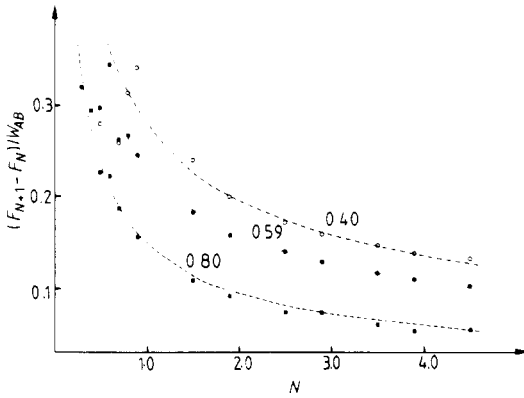


Figure 1. $(F_{N+1} - F_N)/W_{AB}$ at three reduced temperatures: $T/T_c = 0.40, 0.59$ and 0.80 , as a function of the number N of B particles in the cluster. The curves are computed according to equations (14) and (15). The size of the symbols representing the experimental data ranges from 4 times to twice the experimental uncertainty.

Clearly $\tau = 1.25$ gives a good fit of equation (14) to the data. Table 4(a) shows the values of τ together with their uncertainty deduced from fitting equation (14) to the data, with a and b given the value of table 3. As can be seen, τ is certainly not of the order of 2 (Fisher 1967) but is very close to 1.25 (Wallace 1981, 1982, Lowe and Wallace 1980).

Conversely, assuming $\tau = 1.25$, we can check for the consistency of the measured surface specific free energy with the value predicted by Zia and Avron (1982). This is done by fitting equation (14) to the data, with $\tau = 1.25$ and a being given the value of table 3. As shown in table 4(b), the agreement is excellent. As a by-product, the computation yields the internal energy of the cluster as a function of the cluster size

$$U_N = \langle U(C_N^N) \rangle_N \tag{16}$$

where $U(C_N^N)$ is computed according to equation (2) and the average $\langle \rangle_N$ is taken along the Markov chain generated for the system with N B particles. Table 5 gives the results. New information may be extracted from this direct independent measurement of U_N . Indeed, since

$$U_N = \partial(\beta F_N) / \partial \beta \tag{17}$$

Table 4. Check for the choice of τ in equation (14).

(a) Values of τ obtained giving a and b (equation (15)) their theoretical value.

T/T_c	0.801	0.588	0.401
τ	1.02 ± 0.19	1.27 ± 0.18	1.30 ± 0.44

(b) Value of b in equation (14) obtained giving a and τ their theoretical value (equation (15)), and value of b' in equation (19) compared to the prediction of equation (20).

T/T_c	0.801	0.588	0.401
b_{measured}	0.625 ± 0.031	1.250 ± 0.026	1.650 ± 0.045
$b_{\text{eqn(15)}}$	0.665	1.251	1.645
b'_{measured}	3.29 ± 0.01	2.70 ± 0.01	2.37 ± 0.01
$b'_{\text{eqn(20)}}$	3.10	2.68	2.35

Table 5. Measured values of U_N (equation (16)) and deviation from the value predicted by equations (19)–(20): $\Delta' = U_N$ (measured) – U_N (equation (19)); d' (equation (21)) is the average value of Δ' .

N	$T/T_c = 0.801$		$T/T_c = 0.588$		$T/T_c = 0.401$	
	U/W_{AB} (eqn (16))	Δ/W_{AB}	U/W_{AB} (eqn (16))	Δ'/W_{AB}	U/W_{AB} (eqn (16))	Δ'/W_{AB}
15	10.744 ± 0.016	-1.854	9.603 ± 0.010	-0.850	8.635 ± 0.010	-0.483
16	11.173 ± 0.016	-1.858	9.949 ± 0.010	-0.849	8.993 ± 0.010	-0.424
19	12.442 ± 0.016	-1.819	10.936 ± 0.011	-0.841	9.820 ± 0.010	-0.442
20	12.830 ± 0.020	-1.821	11.221 ± 0.012	-0.864	10.065 ± 0.010	-0.464
25	14.756 ± 0.021	-1.727	12.711 ± 0.013	-0.817	11.360 ± 0.012	-0.423
26	15.096 ± 0.022	-1.733	12.972 ± 0.014	-0.826	11.606 ± 0.012	-0.400
29	16.154 ± 0.024	-1.679	13.742 ± 0.015	-0.840	12.246 ± 0.011	-0.434
30	16.576 ± 0.030	-1.581	14.014 ± 0.015	-0.820	12.460 ± 0.012	-0.437
35	18.205 ± 0.033	-1.507	15.205 ± 0.015	-0.833	13.491 ± 0.014	-0.440
36	18.505 ± 0.034	-1.506	15.490 ± 0.015	-0.778	13.707 ± 0.013	-0.422
39	19.446 ± 0.036	-1.442	16.126 ± 0.016	-0.816	14.246 ± 0.013	-0.460
40	19.665 ± 0.040	-1.518	16.356 ± 0.020	-0.805	14.449 ± 0.015	-0.445
45	21.164 ± 0.040	-1.393	17.444 ± 0.020	-0.773	15.353 ± 0.015	-0.445
46	21.505 ± 0.040	-1.321	17.645 ± 0.020	-0.776	15.530 ± 0.015	-0.443
Average value of Δ'/W_{AB}		-1.626		-0.821		-0.440

and writing with the notations of equation (14)

$$F_N/W_{AB} = aN + bN^{1/2} + (\beta W_{AB})^{-1} \tau \ln(N/C_{\text{coex}}) \quad (18)$$

we get

$$U_N/W_{AB} = a'N + b'N^{1/2} + c' \quad (19)$$

with

$$a' = a \left(1 + \frac{\partial \ln a}{\partial \ln \beta} \right) \quad b' = b \left(1 + \frac{\partial \ln b}{\partial \ln \beta} \right) \quad c' = \frac{\tau \partial \ln C_{\text{coex}}}{W_{AB} \partial \beta} \quad (20)$$

In equations (19) and (20), a' , b' , c' may be given the theoretical values deduced from equation (15) and the theoretical expression of μ_{coex} , C_{coex} given in appendix 1. The surface specific potential energy ($\partial \beta \Sigma / \partial \beta$) has been computed by the numerical derivation of Σ . The important result is that U_N/W_{AB} thus computed is always larger than the measured value (table 5) by a quantity which is almost size independent. It is therefore tempting to write

$$U_N/W_{AB} = a'N + b'N^{1/2} + c' + d' \quad (21)$$

which would result in the following expression for the free energy F_N

$$F_N/W_{AB} = aN + bN^{1/2} + (\beta W_{AB})^{-1} \tau \ln(N/C_{\text{coex}}) + d. \quad (22)$$

In equations (21) and (22), d' and d are related by

$$d' = \partial(\beta d) / \partial \beta. \quad (23)$$

Obviously the term d does not appear in $F_{N+1} - F_N$ which is the measured quantity. The term d in equation (22) can be simply interpreted as a curvature dependence of

the surface specific free energy. Indeed, writing

$$\Sigma = \Sigma_{\infty}(1 + \epsilon N^{-1/2}) \tag{24}$$

yields from equation (15)

$$d = (\epsilon \Sigma_{\infty} / W_{AB}) C_{\text{coex}}^{-1/2}. \tag{25}$$

A curvature dependence of Σ is predicted on the basis of the Gibbs thermodynamic description of capillarity, although this sign of the effect is controversial (Tolman 1949, Kirkwood and Buff 1949, Oriani and Sundquist 1963). The value of ϵ follows from equation (25) once d is known. d could in principle be obtained from d' by integration of equation (23). However, we miss a reference state for this integration to be performed. Nevertheless, for small clusters, we may obtain F_N by summation of $F_{N+1} - F_N$ starting from $N = 1$ where Q_N is known exactly. As can be seen in table 6, the measured values are always larger than the values predicted by equation (18), by a quantity which remains essentially constant for cluster sizes larger than 8. The constants d thus obtained yield \tilde{d}' values according to equation (23) which compare very well with the d' values measured directly (table 6). The interesting result is that d is positive, suggesting an increase in surface tension with increasing curvature, the effect being larger the larger the temperature.

Table 6. Estimation of the constant d in F_N (equation (22)) from the difference $\Delta = F_N$ (measured) - F_N (equation (14)). F_N (measured) = $F_1 + \sum_{i=1}^{N-1} (F_{i+1} - F_i)$. The constant d (equations (22), (25)) is the average value of Δ . Value of d' deduced from d by equation (23) and comparison with the value of d' measured directly (table 5). ϵ in the last line follows from equations (15) and (25): $\epsilon = d/b$.

T/T_c	0.801	0.588	0.401
N			
8	1.429	0.713	0.289
9	1.427	0.716	0.286
10	1.423	0.715	0.329
d	1.426	0.715	0.301
\tilde{d}' eqn (23)	-1.800	-0.902	-0.380
c' eqn (20)	-0.0785	-0.0088	-0.00041
$(c' + d')$ calc.	-1.8785	-0.9108	-0.3804
$(c' + d')$ exp.	-1.63	-0.82	-0.44
ϵ	2.14	0.57	0.18

5. Summary and conclusion

The computational algorithm we have constructed yields a direct and efficient way for calculating the free energy difference of clusters of neighbouring size: $F_{N+1} - F_N$. Using a reasonable amount of computer time, an accuracy consistently better than 2.5% and usually better than 1% may be reached for cluster sizes up to 45 particles at temperatures of $0.8T_c$. The present work offers one more example of the efficiency of computer calorimetry techniques for computing free energy differences.

The results ($F_{N+1} - F_N$, $1 < N < 45$, $0.4 \leq T/T_c \leq 0.8$) have been compared to the value of F_N derived from a capillarity model where care is taken to evaluate all terms exactly. In the capillarity approximation, the free energy of a cluster is assumed to be that of a large equilibrium precipitate: the bulk term is the free energy per particle in the bulk precipitate, the surface term is the surface specific free energy of a large precipitate which has achieved its equilibrium shape. The logarithmic correction is included. All the terms of the capillarity model are given the theoretical value derived from the exact solution (or low-temperature expansion) of the 2D square Ising model with nearest-neighbour interactions. An excellent agreement with the raw data is found, provided that the coefficient of the logarithmic term is given the value 1.25 predicted recently (Wallace 1981, 1982, Lowe and Wallace 1980) instead of 2.067 which was derived from scaling arguments near T_c (Fisher 1967). The ability of the correctly evaluated capillarity model to describe ($F_{N+1} - F_N$) is surprisingly good down to cluster sizes of $N \sim 10$.

However, the direct computation of the internal energy U_N of the clusters as a function of their size N , as well as the evaluation of F_N by summation of $F_{N+1} - F_N$ for $1 < N < 10$, suggests that the surface specific free energy of the model is curvature dependent: it increases with increasing temperature.

The technique developed in this work is very efficient and should be usefully applied to other models of interest.

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Appendix 1. Correspondence between the binary alloy and magnetic interpretations of the Ising model

For a given configuration of the spins $\{\sigma_i\}$, the Ising energy is

$$E_I^N = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - mH \sum_i \sigma_i$$

where σ_i can take the values ± 1 , m is the magnetic moment and H is the magnetic field; the sum is extended to all first-neighbour pairs. The canonical partition function for N spins at temperature $T = 1/k_B\beta$ is

$$Z_I^N = \sum_{\sigma_1} \sum_{\sigma_2} \dots \sum_{\sigma_N} \exp\left(\beta J \sum_{\langle ij \rangle} \sigma_i \sigma_j + \beta mH \sum_i \sigma_i\right)$$

where the σ 's take up their two possible values.

Let us write the alloy energy as

$$E_A^N = \sum_{\langle ij \rangle} [\varepsilon_{AA} C_i^A C_j^A + \varepsilon_{AB} (C_i^A C_j^B + C_i^B C_j^A) + \varepsilon_{BB} C_i^B C_j^B]$$

where $C_l^A = 1$ and $C_l^B = 0$ if site l is occupied by A and $C_l^A = 0$ and $C_l^B = 1$ otherwise.

If we let $C_l^A = \frac{1}{2}(1 + \sigma_l)$, $C_l^B = \frac{1}{2}(1 - \sigma_l)$ we get

$$E_A^N = -\frac{1}{4}(2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB}) \sum_{(ij)} \sigma_i \sigma_j - (\varepsilon_{BB} - \varepsilon_{AA}) \sum_i \sigma_i + \frac{1}{2}N(2\varepsilon_{AB} + \varepsilon_{AA} + \varepsilon_{BB}).$$

The number N_A of atoms of type A is $\sum_i C_i^A = \frac{1}{2}N + \frac{1}{2}\sum_i \sigma_i$ and the number N_B of atoms of type B is $\sum_i C_i^B = \frac{1}{2}N - \frac{1}{2}\sum_i \sigma_i$. The grand partition function Ξ_A^N for the alloy with N sites at chemical potentials μ_A and μ_B and temperature $T = 1/k_B\beta$, is

$$\begin{aligned} \Xi_A^N &= \sum_{\sigma_1} \dots \sum_{\sigma_N} \exp[-\beta(E_A^N - N_A\mu_A - N_B\mu_B)] \\ &= \exp\{\beta\frac{1}{2}N[\mu_A + \mu_B - (2\varepsilon_{AB} + \varepsilon_{AA} + \varepsilon_{BB})]\}. \end{aligned}$$

Calling

$$\Lambda_0 = \exp\{\beta[\mu_A + \mu_B - (2\varepsilon_{AB} + \varepsilon_{AA} + \varepsilon_{BB})]/2\}$$

we have

$$\Xi_A^N = \Lambda_0^N Z_1^N \quad (\text{A1.1})$$

and

$$E_A^N = E_1^N + \frac{1}{2}(\mu_A - \mu_B) \sum_i \sigma_i + \frac{1}{2}N(\varepsilon_{AA} + 2\varepsilon_{AB} + \varepsilon_{BB}),$$

if we let

$$4J = 2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB}$$

and

$$mH = (\mu_A - \mu_B)/2 + \varepsilon_{BB} - \varepsilon_{AA}.$$

If we now take $\varepsilon_{AA} = \varepsilon_{BB} = 0$, we see that the zero-field solution of the Ising model corresponds to $\mu_A = \mu_B = \mu_{\text{coex}}$ for the alloy, μ_{coex} being the common value of the chemical potentials on the coexistence line. The two systems differ for a constant term in the internal energy

$$E_A^N = E_1^N + N\varepsilon_{AB}.$$

Taking the logarithm of equation (A1.1) and remembering that in zero field the Helmholtz free energy is equal to the Gibbs free energy we get:

$$-(1/\beta) \ln \Xi_A^N = F - G = 0 = -N\mu_{\text{coex}} + N\varepsilon_{AB} - (1/\beta) \ln Z_1^N$$

and

$$\mu_{\text{coex}} = -(1/\beta N) \ln Z_1^N + \varepsilon_{AB}$$

so that the free energy differs in the two systems by the same constant as the internal energy.

At zero field, μ_{coex} is given by the following low-temperature expression (Sykes *et al* 1965)

$$\beta\mu_{\text{coex}} = -u^2(1 + 2u + 4\frac{1}{2}u^2 + 12u^3 + \dots)$$

with

$$u = \exp -2\beta\varepsilon_{AB}$$

while the concentration is

$$C_{\text{coex}} = 1 - u^2(1 + 4u + 17u^2 + 76u^3 + \dots).$$

The equilibrium shape of a drop in the 2D Ising model is given by

$$\cosh \zeta \cosh \eta = \frac{1}{2} \cosh 2\beta J \coth 2\beta J \quad (\text{A1.2})$$

where ζ and η are coordinates along $\langle 111 \rangle$ directions ($\beta(x \pm y)/2$, x and y being the coordinates along $\langle 010 \rangle$ directions). The surface energy of a drop of N sites grows as $N^{1/2}$, the proportionality constant being

$$\Sigma = 2W^{1/2}$$

where W is the area included in the equilibrium contour given by (A1.2) (Zia and Avron 1982).

Appendix 2. The method of overlapping distributions

Consider two systems: A and B , having different Hamiltonians but defined on the same configuration space. Let $F_\alpha = -kT \ln Q_\alpha$ be the free energy of system α ($\alpha = A$ or B) and Q_α be the configurational integral

$$Q_\alpha = \sum_i \exp -\beta U_\alpha(C_i).$$

Then

$$\begin{aligned} \exp[-\beta(F_B - F_A)] &= Q_B/Q_A = \left[\sum_i \exp -\beta U_B(C_i) \right] / \left[\sum_i \exp -\beta U_A(C_i) \right] \\ &= Q_A^{-1} \sum_i \exp -\beta [U_B(C_i) - U_A(C_i)] \exp -\beta U_A(C_i) \\ &= \langle \exp -\beta (U_B - U_A) \rangle_A \\ &= Q_B / \left\{ \sum_i \exp -\beta [U_A(C_i) - U_B(C_i)] \exp -\beta U_B(C_i) \right\} \\ &= \langle \exp \beta (U_B - U_A) \rangle_B^{-1}. \end{aligned}$$

We see that the free energy difference between the two systems can be obtained as a thermal average in the form of 'one-sided evaluations', i.e. in the form of thermal averages in one of the two canonical ensembles.

A two-sided evaluation can be also obtained. Let us introduce the fraction $f_\alpha(\Delta)$ of the configurations having the value Δ for $U_B - U_A$ in ensemble α

$$\begin{aligned} f_A(\Delta) &= Q_A^{-1} \Sigma \{ \delta[\Delta - U_B(C_i) + U_A(C_i)] \exp[-\beta U_\alpha(C_i)] \} \\ f_B(\Delta) &= Q_B^{-1} (\exp -\beta \Delta) \Sigma \{ \delta[\Delta - U_B(C_i) + U_A(C_i)] \exp[-\beta U_A(C_i)] \} \\ &= Q_A Q_B^{-1} (\exp -\beta \Delta) f_A(\Delta). \end{aligned}$$

We then obtain

$$\exp -[\beta(F_B - F_A)] = Q_B/Q_A = (\exp -\beta \Delta) f_A(\Delta) / f_B(\Delta).$$

The advantage of the above two-sided evaluation consists in the possibility of obtaining accurate evaluations of the free energy difference when the two distributions $f_A(\Delta)$

and $f_B(\Delta)$ obtained numerically as histograms in Monte Carlo runs, overlap only partly. In fact, in this case the one-sided evaluation will be strongly in error; on the contrary the two-sided evaluation will not suffer from the overlap region being restricted to a portion of the intervals where $f_A(\Delta)$ and $f_B(\Delta)$ are numerically appreciable.

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