

Clusters, Metastability, and Nucleation: Kinetics of First-Order Phase Transitions

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We describe and interpret computer simulations of the time evolution of a binary alloy on a cubic lattice, with nearest neighbor interactions favoring like pairs of atoms. Initially the atoms are arranged at random; the time evolution proceeds by random interchanges of nearest neighbor pairs, using probabilities compatible with the equilibrium Gibbs distribution at temperature T . For temperatures $0.59T_c$, $0.81T_c$, and $0.89T_c$, with density ρ of A atoms equal to that in the B-rich phase at coexistence, the density C_l of clusters of l A atoms approximately satisfies the following empirical formulas: $C_1 \approx w(1 - \rho)^3$ and $C_l \approx (1 - \rho)^3 Q_l w^l$ ($2 \leq l \leq 10$). Here w is a parameter and we define $Q_l = \sum_K e^{-\beta E(K)}$, where the sum goes over all translationally nonequivalent l -particle clusters and $E(K)$ is the energy of formation of the cluster K . For $l > 10$, Q_l is not known exactly; so we use an extrapolation formula $Q_l \approx A w_s^{-l} l^{-\alpha} \exp(-bl^\nu)$, where w_s is the value of w at coexistence. The same formula (with $w > w_s$) also fits the observed values of C_l (for small values of l) at densities greater than the coexistence density (for $T = 0.59T_c$): When the supersaturation is small, the simulations show apparently metastable states, a theoretical estimate of whose lifetime is compatible with the observations. For higher supersaturation the system is observed to undergo a slow process of segregation into two coexisting phases (and w therefore changes slowly with time). These results may be interpreted as a more quantitative formulation (and confirmation) of ideas used in standard nucleation theory. No evidence for a "spinodal" transition is found.

KEY WORDS: Cluster destruction; metastable states; nucleation kinetics; computer simulation; lattice gas; binary alloy.

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1. INTRODUCTION

The object of this paper is to summarize and interpret the results of some computer simulations which demonstrate, among other things, the possibility of metastable states in a binary alloy (and in the corresponding lattice gas).

In earlier papers of this series⁽¹⁻⁴⁾ we described the results of computer simulations of the time evolution of such an alloy following quenching from a high temperature (where the equilibrium state is spatially uniform) to a low temperature for which the equilibrium state has comparable amounts of two different phases. In following the system's evolution (at the lower temperature) from the initial "macroscopically" uniform state to a state in which there are distinct regions containing A-rich and B-rich phases, our main tool was the Fourier transform of the pair correlation function. In the present paper we summarize and interpret the results of simulations where the true equilibrium state after quenching still has two phases, but only a small amount of one of them. In the language of the density-temperature diagram, we are still quenching to points inside the two-phase region, but they are now close to the coexistence curve. This part of the diagram is called the nucleation region. Our tool for investigating the time evolution is now the analysis of clusters of the minority atoms.

We find that at points close to the coexistence curve (i.e., small supersaturation in the lattice gas language) the system can stay for very long times in a metastable state of uniform macroscopic density. As the supersaturation is increased, the rate at which nucleation and segregation of the new phase take place increases in an apparently continuous fashion until we find ourselves in the rapidly varying regime studied earlier. No sharp "spinodal transition" from metastable to unstable states was observed, although the probability of nucleating a critical cluster changes rapidly with the degree of supersaturation. This fits in with our earlier findings that the Cahn-Hilliard *linearized* theory,⁽⁵⁾ which among other things also predicts such a transition, does not yield a good description of the computer simulations. Similar conclusions have also been drawn by other authors^(6,7) on the basis of both theory and experiment.

The simulations were done on the CDC 6600 computer at the ERDA Mathematics and Computer Laboratory at New York University. The program simulates a simple cubic lattice of N sites (where $N = 125 \times 10^3$ or 27×10^3) with periodic boundary conditions, each site of the lattice having two states, "occupied" and "unoccupied" (in the interpretation appropriate for alloys, an "occupied" site holds an A atom and an "unoccupied" site holds a B atom). At the initial time, a specified number ρN of randomly chosen sites are put in the "occupied" state and the rest in the "unoccupied" state. The program chooses a pair of neighboring sites at random, then

exchanges their occupation states (i.e., the atoms on them) with a probability given by

$$[\exp(-\beta \Delta E)]/[1 + \exp(-\beta \Delta E)] \quad (1)$$

where $\beta = 1/kT$ is a constant and ΔE is the increase in energy caused by the interchange. The energy is defined as

$$E = -V \sum_{i,j} n_i n_j, \quad n_i = 0,1 \quad (2)$$

where V is a constant, n_i is the occupation number of the i th site, and the sum goes over all nearest neighbor pairs of sites. The transition probability (1) satisfies the detailed balancing condition for equilibrium at temperature $1/k_B\beta$.

As the simulation proceeds, the computer periodically records information about the current configuration. In particular, it calculates the sizes of all the clusters (maximal connected sets of occupied sites) in the configuration. This information about clusters yields, at low densities, a description of the configurations which provides a convenient way to understand what is going on, and makes possible some quantitative comparisons between theory and simulation.

2. QUALITATIVE DESCRIPTION OF THE DATA

Most of the simulation runs reported on here were done at a temperature T such that $\beta V = 1.5$; that is, $T = 0.59T_c$, where T_c is the critical temperature, which is known very accurately from series expansions.⁽⁸⁾ The lowest density studied was $\rho = 0.0146$, which, according to the Padé approximant formula,⁽⁸⁾ is the saturated vapor density at this temperature. The simulation runs at this density show, as we would expect, a distribution of cluster sizes which varies rapidly at first, since the initial random state corresponds to equilibrium at infinite temperature rather than at $0.59T_c$, but soon settles down (after about 50 attempted exchanges per site) to an equilibrium in which no cluster of more than 11 particles was ever observed.

At the next density, 0.02, the behavior is qualitatively very similar, but with somewhat more clusters of each size than at density 0.0146. The largest cluster observed among the configurations recorded contained 26 particles, and clusters of this size usually lasted only a short time. There was no observable tendency for the cluster distribution to change with time (apart from fluctuations) and since this state has a higher density than that of the standard "vapor" phase, we interpret it as a metastable state.

At the next density studied, $\rho = 0.035$, the distribution of small clusters appears to reach equilibrium in about the same time as before, 50–100

attempted exchanges per site; but it takes longer (about 400 attempted exchanges per site) for the number of clusters in the size range 30–50 to build up. By the end of the run (about 450 attempted exchanges per site) the number of clusters in this size range appeared to be fairly steady, but the runs were not long enough to decide definitely whether the state at this density could be regarded as metastable.

At densities 0.05 and 0.06, a new pattern of behavior is beginning to show itself. Once again a fairly stable distribution of cluster sizes is established after about 50–100 attempted exchanges per site, but now this distribution is itself slowly changing with time: The number of large clusters (larger than, say, 50) is seen to build up slowly with time, as is the number of particles in such clusters, while the number of particles in small clusters (ten particles or less) can be seen, despite the fluctuations, to be decreasing steadily on the average. Thus, in the $\rho = 0.05$ case the total number of particles in clusters of ten or fewer particles decreases from about 5400 (i.e., 0.043 per site) after 100 attempted exchanges per site to about 4800 (i.e., 0.035 per site) after 500 attempted exchanges per site; and in the $\rho = 0.06$ case the same effect was even more marked. For the $\rho = 0.075$ case we made one much longer run, lasting for nearly 6500 attempted exchanges per site. By the end of this run, the distribution of small clusters was no longer changing rapidly, the number of particles in such clusters having settled down at about 2700 (i.e., 0.022 per site), and the remaining particles had arranged themselves into about 25 large clusters ranging in size from about 100 particles to about 750. Very slowly, the smallest clusters among these were shrinking or breaking up and the largest were growing, a phenomenon known as Ostwald ripening in the metallurgical literature. At these densities, therefore, it is no longer a question of metastability; rather, we are witnessing the formation of nuclei of the high-density phase, which come to an approximate steady state with the low-density phase. The density of this low-density phase exceeds the saturated vapor pressure because the vapor pressure over a convex surface, such as that of a 750-particle droplet or cluster, is higher than that over a flat surface.

The last density studied in some detail in this series of simulations at $T = 0.59T_c$ was $\rho = 0.1$. The phenomena appear to be similar to those at $\rho = 0.075$, but they happen still more rapidly. The speed of the process grew further as the density was increased to $\rho = 0.12$, where only short runs were made.

The phenomena thus appear to go over continuously into what was observed at the much higher density $\rho = 0.2$, which was studied in another series of simulations⁽⁴⁾ at the same temperature. Here the system came fairly quickly to a state which was characterized by a “gas” phase containing small clusters of size ≤ 10 , one or two “giant” clusters (over 4000 particles) containing about half the particles, and some intermediate clusters of sizes

between 10 and 1000 whose number decreases fairly steadily with the progress of time. The results of this simulation are thus consistent with our results for the cluster size distributions at lower densities. We have not, however, attempted a quantitative analysis of the cluster distribution at density 0.2 because at such high densities it is not clear that we can assign all the large clusters to the high-density phase: Even at infinite temperature, where there is certainly only one phase, large clusters appear as soon as the density increases toward the percolation density, which is about 0.31 for this lattice. Beyond this density there will be a cluster of size proportional to the size of the system.⁽⁹⁾

3. EQUILIBRIUM CLUSTER DISTRIBUTIONS

As a first step toward a quantitative theory of the phenomena observed in the simulation, we should like to have a theoretical expression for the equilibrium distribution of the sizes of small clusters at various temperatures and densities. At very low densities we could use the upper and lower bounds given by Lebowitz and Penrose,⁽¹⁰⁾ but at the densities we are interested in these bounds are not close enough together to give accurate information, particularly for the larger clusters. Accordingly, we shall instead use an empirical formula.

A useful empirical formula is suggested by the lower bound on C_l , the equilibrium number of l -particle clusters per site, given in Eq. (30) of Ref. 10; for a simple cubic lattice this bound is

$$C_l \geq Q_l [z(1 - \rho)^5]^l (1 - \rho)^2 \quad (3)$$

where Q_l is the "cluster partition function" defined by

$$Q_l = \sum_K e^{-\beta E(K)} \quad (4)$$

Here the sum includes just one member from each set of translationally non-equivalent l -particle clusters, and $E(K)$ is the (negative) energy of the cluster K . The form of Eq. (3) suggested looking for an approximation of the form

$$C_l \simeq Q_l w^l (1 - \rho)^k \quad (5)$$

where w depends on z (i.e., on ρ) but $Q_l = Q_l(\beta)$ does not. This formula would imply that the quantities C_1/Q_1 , C_2/Q_2 , C_3/Q_3 , ... form a geometrical progression with common ratio w . The values observed at equilibrium, at the three different temperatures studied, did form approximate geometrical progressions, with the exception of the first member C_1/Q_1 in each case. The appropriate value of k was about 4. To fit the observed values of C_1/Q_1 ,

Table I. Test of the Empirical Formula for C_l at Saturation Densities

Temperature	$0.59T_c$		$0.81T_c$		$0.89T_c$	
βV	1.500		1.09428		1.000	
Density	0.0146		0.075		0.1272	
w	0.010526		0.029837		0.035247	
	Observed	Formula	Observed	Formula	Observed	Formula
C_1	0.010126	0.010071	0.023370	0.023615	0.023002	0.023435
C_2	0.001382	0.001404	0.005944	0.005840	0.006060	0.005879
C_3	0.000328	0.000331	0.002582	0.002603	0.002673	0.002817
C_4	0.000102	0.000100	0.001388	0.001422	0.001621	0.001640
C_5	0.000035	0.000034	0.000870	0.000867	0.000940	0.001063
C_6	0.000013	0.000013	0.000549	0.000566	0.000716	0.000734
C_7	0.000006	0.000005	0.000395	0.000387	0.000525	0.000531
C_8	0.000002	0.000002	0.000278	0.000274	0.000459	0.000397
C_9	0	0.000001	0.000210	0.000199	0.000336	0.000304
C_{10}	0	0.000000	0.000163	0.000148	0.000294	0.000237
$\sum_{i=1}^{10} l c_i$	0.014593	0.014580	0.064709	0.064695	0.071932	0.071923

however, it was necessary to take k to be about 3, rather than 4, when $l = 1$. The empirical formulas we shall use are thus (since $Q_1 = 1$)

$$C_1 = w(1 - \rho)^3, \quad C_l = Q_l w^l (1 - \rho)^4, \quad l \geq 2 \quad (6)$$

(A somewhat better fit with the data can be obtained by using the exponents 3.1 and 3.9, but the improvement is hardly great enough to justify using nonintegral exponents.) Provided $w \geq z(1 - \rho)^{-4}$, the approximate formulas (6) are consistent with the rigorous inequality (3), and if $w = z(1 - \rho)^{-4}$, the approximate formula is correct to the lowest two orders in ρ when $l = 1$ or 2. However, the actual values of w that fitted the data best were closer to $z(1 - \rho)^{-3}$ than to $z(1 - \rho)^{-4}$.

Table I gives the observed cluster distributions for the saturated "vapor" phase at three temperatures $0.59T_c$, $0.81T_c$, and $0.89T_c$, together with values given by the empirical formulas. The value of w was chosen so as to make the total number of particles in clusters of sizes from one to ten, as given by the empirical formulas, equal to the observed number of particles in such clusters. The significance of the number ten is that we have exact formulas for Q_l with $l \leq 10$; these were kindly supplied by M. Sykes.

4. LARGER CLUSTERS AT EQUILIBRIUM

To study metastability and nucleation we want to use the empirical formulas (6) for values of l considerably greater than ten, and to do this we

need values of Q_l for those values of l . Since these are not known exactly, we have estimated them using an extrapolation formula of the form suggested by Fisher,⁽¹¹⁾

$$Q_l = Al^{-\tau} \exp(al - bl^\sigma) \quad (7)$$

where A , τ , σ , a , and b are constants. The value of a was obtained by assuming that the radius of convergence of the approximate series for the density,

$$\rho = w(1 - \rho)^3 + \sum_{l=2}^{\infty} Q_l w^l (1 - \rho)^4 \quad (8)$$

was exactly equal to w_s , the value of w for the saturated vapor; that is, we took $a = -\log w_s$. The other constants A , τ , b , and σ were chosen so as to give a good fit to the known values of Q_3, \dots, Q_{10} (we excluded Q_1 and sometimes Q_2 because this made possible a much better fit to the remaining Q_l).

At the temperature $0.59T_c$, where all our simulation runs at super-saturated densities were made, it turned out that a good fit could be obtained for $3 \leq l \leq 10$ with

$$\sigma = 5/8, \quad \tau = 0, \quad b = 3, \quad A = e^{-2} = 0.1353$$

giving the extrapolation formula

$$Q_l \simeq w_s^{-1} \exp(-2 - 3l^{5/8}) \quad (T = 0.59T_c) \quad (9a)$$

with $w_s = 0.010526$.

For the other two temperatures considered here, the corresponding formulas (which give Q_3, \dots, Q_{10} with an accuracy of about 1%) are given by

$$Q_l \simeq w_s^{-1} \exp(0.965 - 4.75l^{0.3}) \quad (T = 0.81T_c) \quad (9b)$$

$$Q_l \simeq w_s^{-1} \exp(2.82 - 6.4l^{0.22}) \quad (T = 0.89T_c) \quad (9c)$$

An equally good fit to the known Q_l , $3 \leq l \leq 10$, and to Q_2 as well, can be obtained by setting in (7) $\sigma = 16/25 = 0.64$, the value suggested by Fisher, and just varying A , τ , and b . We find, then,

$$w_s^l Q_l \simeq \begin{cases} l^{-0.461} \exp(-2.11 - 2.63l^{0.64}), & T = 0.59T_c & (10a) \\ l^{-1.37} \exp(-3.08 - 0.52l^{0.64}), & T = 0.81T_c & (10b) \\ l^{-1.42} \exp(-3.1 - 0.324l^{0.64}), & T = 0.89T_c & (10c) \end{cases}$$

If we require τ to have the value 2.2 suggested by Fisher (for $T \rightarrow T_c$, $l \rightarrow \infty$), however, then the fit is not so good. The inadequacy of a formula of this type with $\tau = 2.2$ for representing the observed concentrations of large clusters has already been noted by Müller-Krumbhaar and Stoll.⁽¹²⁾

A test of our extrapolation formulas (10a)–(10c), assuming that (6) hold well also for $l > 10$, is given in Table II. The test gives rather good agreement for the temperature $0.81T_c$, but for $T = 0.89T_c$ the predictions of the

Table II. Test of the Extrapolated Formula for C_l at Saturation Density for Various Temperatures^a

Temperature		0.59 T_c		0.81 T_c		0.89 T_c	
βV		1.5		1.09428		1	
Density		0.0146		0.075		0.1272	
w_s		0.010526		0.029837		0.035247	
p	q	Observed	Formula	Observed	Formula	Observed	Formula
		$\sum C_l$					
1	10	0.0146	0.0146	0.06481	0.06471	0.07260	0.07194
11	11	0	0.00000	0.00127	0.00123	0.00235	0.00209
12	13			0.00200	0.00192	0.00433	0.00349
14	15			0.00147	0.00140	0.00387	0.00279
16	18			0.00157	0.00147	0.00497	0.00326
19	22			0.00134	0.00125	0.00561	0.00318
23	27			0.00098	0.00093	0.00539	0.00279
28	32			0.00057	0.00055	0.00428	0.00196
33	38			0.00040	0.00040	0.00463	0.00168
39	46			0.00028	0.00030	0.00426	0.00152
47	55			0.00015	0.00018	0.00321	0.00113
56	66			0.00008	0.00011	0.00300	0.00090
67	79				0.00006	0.00270	0.00067
80	95				0.00004	0.00198	0.00051
96	114				0.00002	0.00134	0.00036
115	137				0.00001	0.00103	0.00025
138	165				0.00000	0.00074	0.00017
1	165	0.0146	0.0146	0.07492	0.07458	0.12629	0.09869

^a Comparison of observed with predicted values for $\sum_{p \leq l \leq q} C_l$, the number of particles per site in clusters of between p and q .

extrapolation formula are too small by a factor of about four for the largest clusters. This may be due to the fact that at this temperature we are just on the borderline where percolation occurs⁽¹³⁾ and our formulas (6) are not likely to be a good approximation for large l when that happens. For $T = 0.59T_c$ no test is possible since the concentrations of large clusters are too small to measure.

Similar fits could be obtained also by setting $\sigma = 2/3$, its "classical" value. We shall not discuss these extrapolation formulas further here, as they only affect the C_l for $l > 10$, where our analysis is in any case only qualitative.

We should note here that our assumption, also made in the droplet model,⁽¹¹⁾ that C_l does not decay exponentially fast in l on the coexistence line has been recently proven rigorously by Kunz and Souillard.⁽¹⁴⁾

5. METASTABLE STATES

The observations described in Section 2 indicate that at the temperature $0.59T_c$ and the density 0.02 the system studied here can exhibit a metastable

state, in which the distribution of clusters is qualitatively similar to that in the saturated vapor. The system changes very slowly with time, if at all; yet the density is higher than the saturated vapor density at the temperature considered, so that the true equilibrium state should have two phases, one of which would show itself as at least one very large cluster. In this section we show that the approximate formulas of the preceding two sections make possible an approximate quantitative description of these metastable states. We are assuming, here, and this seems very likely, that our system is sufficiently large to exhibit "macroscopic" behavior, i.e., effective segregation into a liquid and a vapor phase.

A metastable vapor phase is one in which the density is higher than in the saturated vapor, but in which the high-density phase forms very slowly because clusters large enough to nucleate its growth, i.e., $l > l^*$ (the "critical" cluster size), form only very rarely. One way of calculating the properties of the metastable state^(15,16) is to represent it by a restricted equilibrium ensemble constructed from the canonical or grand canonical ensemble by excluding all systems containing clusters larger than the critical size l^* . We shall assume that if l^* is not too small, the equilibrium concentrations C_i in such an ensemble can be calculated for $l < l^*$ from our empirical formulas (6). Let us think of any clusters of size exceeding l^* in the actual system (not the restricted ensemble) as being nuclei of the new phase. To obtain a rough estimate of the rate of formation of such nuclei we assume, as is done in standard nucleation theory (see, e.g., Ref. 17), that such a nucleus will be formed every time a cluster of size l^* is found next to a cluster of size l . (We ignore, for this rough calculation, the probability that a nucleus of size l^* will lose a particle.) The probability of this event is proportional to C_l , and also to C_{l^*} . The factor of proportionality may be proportional to some power of l^* , e.g., $(l^*)^{2/3}$, the surface area, but will not depend strongly on C_l , C_{l^*} , or the density. Denoting this factor by K , we obtain the following crude estimate of J , the number of new nuclei of the new phase forming per lattice site per unit time (the unit of time being one attempted interchange per site):

$$J = KC_l C_{l^*} \quad (11)$$

From this formula we can make an estimate of the lifetime of the metastable state; for, as each cluster of the new phase is formed, it takes l^* particles out of the original phase. The number of particles of the original phase therefore changes at an initial rate of roughly Jl^* , and if this rate of change were maintained, the density of the low-density phase would fall from its original value ρ to its equilibrium value ρ_s in a time

$$(\rho - \rho_s)/Jl^* \quad (12)$$

(For a more sophisticated way of computing the lifetime of a metastable state see Ref. 18.)

To use (11) and (12), we want an estimate of the critical cluster size l^* and of its concentration in the metastable state C_{l^*} . For this, we may try the empirical formulas (6). We have already found these formulas to give quite a good fit to the equilibrium cluster distribution at the vapor density $\rho_s(T) = 0.0146$ for $T = 0.59T_c$. Table III shows that the fit is equally good, at least for the clusters of size ≤ 10 , for which we know Q_l exactly, when the density has one of the values (0.02 and 0.035) for which we observed apparently metastable states. For clusters larger than ten particles, we can estimate C_l by assuming that (6) and (9a)–(9c) [which are easier to handle than (10a)–(10c)] hold approximately for $l > 10$, obtaining (for $T = 0.59T_c$).

$$C_l \simeq (1 - \rho)^4 (w/w_s)^l \exp(-2 - 3l^{5/8}) \propto \exp(\lambda l - 3l^{5/8}) \quad (13)$$

with $\lambda = \log(w/w_s)$. Taking for l^* (as is done in standard nucleation theory) the value of l that minimizes C_l , we obtain

$$l^* = (15/8\lambda)^{8/3} \quad (14)$$

and so our best (i.e., smallest) value for C_{l^*} is

$$\begin{aligned} C_{l^*} &= (1 - \rho)^4 \exp[-2 + l^*\lambda - 3(l^*)^{5/8}] \\ &= (1 - \rho)^4 \exp[-2 - (9/8)(15/8\lambda)^{5/3}] \\ &= (1 - \rho)^4 \exp(-2 - 3.2\lambda^{-5/3}) \end{aligned} \quad (15)$$

Table III. Test of the Empirical Formula for C_l at "Metastable" Densities ($T = 0.59T_c$)

l	$\rho = 0.02, w = 0.012888$		$\rho = 0.035, w = 0.016849$	
	C_l		C_l	
	Observed	Formula	Observed	Formula
1	0.012132	0.012131	0.015170	0.015141
2	0.002080	0.002060	0.003307	0.003310
3	0.000588	0.000595	0.001244	0.001250
4	0.000222	0.000221	0.000599	0.000607
5	0.000094	0.000093	0.000328	0.000333
6	0.000042	0.000042	0.000197	0.000199
7	0.000021	0.000021	0.000129	0.000126
8	0.000008	0.000010	0.000085	0.000084
9	0.000005	0.000006	0.000059	0.000058
10	0.000003	0.000003	0.000043	0.000041
$\sum_{l=1}^{10} l c_l$	0.019952	0.019948	0.033278	0.033284

Thus our estimate for the lifetime of a metastable state of density ρ at $T = 0.59T_c$ is, by (11), (12), (14), and (15),

$$\tau \sim [(\rho - \rho_s)/(1 - \rho)^4 K C_1 l^*] \exp(2 + 3.2\lambda^{-5/3}) \quad (16)$$

with l^* and λ as defined above. The most important part of this is the exponential, which can vary over a wide range as a result of quite a small change in w , since $\lambda \rightarrow 0$ as $w \rightarrow w_s$.

The lifetime formula (16) is based on some quite crude approximations, in particular the use of the equilibrium formulas (6) for C_1 , and the neglect of the possibility that a nucleus, once formed, may break up again. One can try to allow for these by using a more detailed model of the kinetics, such as that proposed by Binder *et al.*^(6,18,19) In view of the large uncertainties in the values of C_1 and K , we have not attempted this refinement.

For $\rho = 0.02$ the estimated value of l^* is 378 and the estimated lifetime is about $8 \times 10^{17}/K$ (this is of course a large extrapolation from $l \leq 10$). On the time scale used in our simulations, such a lifetime certainly indicates a metastable state, and even in the real analog of our simulated system, for which our basic time unit might correspond to a small fraction of a second (depending on the temperature and the height of the potential barrier to be overcome in displacing an atom), such a state could have a very long lifetime. For $\rho = 0.035$ the estimated value of l^* is 40 and the estimated lifetime is about $2 \times 10^4/K$. No clusters larger than 40 were observed in the simulation, but since none of the runs lasted more than 500 time units, the theory is consistent with the observations (on the assumption that K is not greater than about 40). For $\rho = 0.05$ the estimated value of l^* is 25, and the estimated lifetime is about $4 \times 10^3/K$. In the simulation at this density, some clusters larger than 25 appeared quite early, and the fraction of particles in such clusters was increasing at a rate of roughly 1.5×10^{-4} per time step. This rate of increase corresponds to a lifetime of about 7×10^3 time steps, and suggests that the value of K is not too far from 1.

For temperatures other than $0.59T_c$ a precisely analogous method for predicting lifetimes can be used; but since we have done no simulations for metastable states at other temperatures, we omit the details.

6. THE GROWTH OF LARGE CLUSTERS

As we have indicated in Section 2, the computer runs for densities 0.05, 0.06, and 0.075 differ on our time scale qualitatively from those made at lower densities. At these densities, the system fairly rapidly forms some large clusters, and these clusters then grow slowly, at the expense of the particles in the small clusters. The nucleation rate is thus too high for the system to be metastable and we are therefore dealing with a time-dependent state of

Table IV. Test of Empirical Formula During Growth of New Phase ($T = 0.59T_c$)

l	$\rho = 0.05,$ $w = 0.018366$ C_l		$\rho = 0.06,$ $w = 0.018816$ C_l		$\rho = 0.075,$ $w = 0.018759$ C_l	
	Observed	Formula	Observed	Formula	Observed	Formula
1	0.015672	0.015746	0.015501	0.015629	0.014698	0.014847
2	0.003704	0.003694	0.003737	0.003717	0.003466	0.003464
3	0.001505	0.001520	0.001574	0.001567	0.001449	0.001456
4	0.000790	0.000804	0.000836	0.000850	0.000778	0.000787
5	0.000494	0.000481	0.000506	0.000521	0.000470	0.000481
6	0.000315	0.000314	0.000354	0.000348	0.000320	0.000320
7	0.000217	0.000217	0.000239	0.000246	0.000227	0.000226
8	0.000159	0.000157	0.000198	0.000183	0.000173	0.000167
9	0.000123	0.000118	0.000144	0.000140	0.000136	0.000128
10	0.000092	0.000091	0.000116	0.000111	0.000114	0.000101
$\sum lC_l$	0.039934	0.039946	0.041408	0.041413	0.038696	0.038696

the system controlled by the growth of large clusters. As a first step toward understanding this process, we may look at the distribution of small clusters to see whether it can still be fitted by the empirical formula (6).

In Table IV the observed concentrations of clusters of up to ten particles, averaged over the time interval 100–600 (the time unit being one attempted interchange per lattice site), are compared with this formula, using the same method as before for choosing w (that the total observed and calculated numbers of particles in these clusters should be equal). The results indicate that we can think of the small clusters as being approximately in equilibrium, but with a value of w which decreases slowly with time. The rate of its decrease is greater, the larger the density, which explains why it is possible for the time average of w for the density 0.075 to be *less* than that for density 0.06 even though the initial value is more.

The next question to be answered is what mechanism determines the value of w , which in turn determines the distribution of small clusters. It appears that the value of w is determined by some average of the size of the large clusters, in accordance with the principle that the vapor pressure over a convex curved surface is larger than the equilibrium vapor pressure. The same idea is of course also used in standard nucleation theory.⁽¹⁷⁾

The calculation of l^* in the preceding section is equivalent to a calculation of the size of a cluster that will, on the average, neither grow nor shrink in the presence of a low-density phase at the given w . Clusters larger than this will tend to grow, absorbing particles from small clusters in the process; clusters smaller than l^* will tend to shrink, evaporating particles

into the "vapor" consisting of the small clusters as they do so. If l^* is smaller than a suitable average of the sizes of the large clusters, then the absorption process will predominate; this will reduce the density of the "vapor" of small clusters, and hence l^* will increase. Likewise, if l^* is too large, it will tend to decrease. Thus the quantity w , which characterizes the quasiequilibrium state of the vapor of small clusters, will adjust itself until the rate of condensation of particles from the "vapor" of small clusters onto clusters that are larger than l^* is just balanced by the rate of evaporation of particles into this "vapor" from clusters that, while smaller than l^* , are still too large to be regarded as part of the "vapor" of small clusters. This regulation mechanism ensures that l^* and w change only very slowly as the result of much slower processes, such as the disintegration or coagulation of large clusters.

The detailed quantitative modeling of this process is, however, beyond the scope of this paper. An attempt in that direction has been made by Binder and co-workers^(6,19) and we intend to return to this point in another publication. The main point, as far as this paper is concerned, is that the distribution of *small* clusters is consistent with the assumption that these clusters are in approximate equilibrium even though the system as a whole is not.

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