

# Monte Carlo Calculation of Phase Separation in a Two-Dimensional Ising System

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Monte Carlo calculations were carried out for a two-dimensional Ising model of a binary alloy with nearest-neighbor attractive interactions between like atoms. The pair correlation observed had the form of an exponentially damped cosine function with parameters varying as the one-sixth power of the time.

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**KEY WORDS:** Monte Carlo; phase separation; two-dimensional Ising; nonequilibrium statistics; spinodal decomposition.

## 1. INTRODUCTION

The Monte Carlo technique has been used rather extensively for investigations of ordering phenomena in two and three dimensions.<sup>(1-6)</sup> In the case of attraction between like, rather than unlike, atoms which results in phase separation rather than ordering, the calculation is a very much slower process and was not suitable for computer investigation until rather recently. Since analytic approximations for the kinetics of phase separation are not completely satisfactory,<sup>(7,8)</sup> and computer capabilities are now adequate, Monte Carlo methods seem appropriate.

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For the initial investigation the two-dimensional rather than the three-dimensional case seemed appropriate. Exact results for the equilibrium structure are known; the results are easily displayed; the amount of computer time required is much less than for the three-dimensional case. As an "experiment" for comparison with analytic approximations, the two-dimensional case is better (in the sense of more severe), since the discrepancy between exact and mean-field theory results for equilibrium properties is so much greater in two dimensions than in three.

## 2. METHOD OF CALCULATION

The method of calculation was similar to that used for various calculations in the ordering case.<sup>(4)</sup> An array in computer memory was created to correspond to a square lattice with cyclic boundary conditions. A "0" was used to represent an "A" atom and a "1" to represent a "B" atom. The dimension of the array was variable, but generally taken as 80 by 80, for a total of 6400 "atoms." Pseudorandom numbers, generated by the multiplicative congruence method,<sup>(7)</sup> were used to provide an initially random configuration of the desired composition, usually equiatomic, and then for decisions for atomic interchange. Direct interchange, rather than vacancy motion, was used to obtain more rapid transformation.

At each step in the calculation a site was chosen at random, and then one of its nearest neighbors was chosen at random. If the two atoms were alike, a new site was chosen. The process was repeated until two unlike nearest neighbors were found. Then the probability of interchange was calculated according to the rule

$$\rho = e^{-\Delta n_{ij}\lambda} / (1 + e^{-\Delta n_{ij}\lambda}) \quad (1)$$

where  $\Delta n_{ij}$  is the change in the number of unlike bonds that would result from the interchange and  $\lambda$  is  $2J/kT$ .

This probability was compared with a random number between zero and one, and if  $\rho$  exceeded the value of the random number, the two atoms were interchanged. The number of tries is proportional to the elapsed time in a real system; we refer to "time" in that sense, with unit time corresponding to one try per site.

After a suitable number of tries the occupancy of the lattice was stored, and the pair correlation was defined by

$$\Gamma(\mathbf{r}) = (4/N) \sum_{\text{sites}} [a(\mathbf{x}) - c][a(\mathbf{x} + \mathbf{r}) - c] \quad (2)$$

where  $\mathbf{x}$  specifies the site,  $\mathbf{r}$  the displacement,  $c$  the fraction of  $B$  atoms (usually  $\frac{1}{2}$ ), and  $a$ , the occupancy (0 for  $A$  atom; 1 for  $B$  atom), was calculated

and stored for all neighbors out to 15 interatomic distances. The “time” was increased after each cycle, since  $t^{1/6}$  dependence was observed, as discussed below. The model is similar to that used by Kawasaki for the study of diffusion in binary systems.<sup>(10)</sup>

### 3. RESULTS

The appearance of the “crystal” in its initial random state, corresponding to a quench from infinite temperature, and after “annealing” at various temperatures below the phase boundary, is shown in Figs. 1–3. Phase separation may be seen to occur by the formation and growth of clusters, but they look rather more like “seaweed” than like the roughly round clusters of traditional theory. The structures look somewhat like those observed in phase-separated glass.<sup>(10)</sup>

The effect of temperature can be seen quite clearly in the later stages of the process. In Fig. 3, where the temperature is well below the critical temperature, the regions are composed of virtually pure *A* and *B*. In Fig. 1, where the temperature is just below the critical, the presence of an occasional *A* atom in a *B* region, and vice versa, is quite evident.

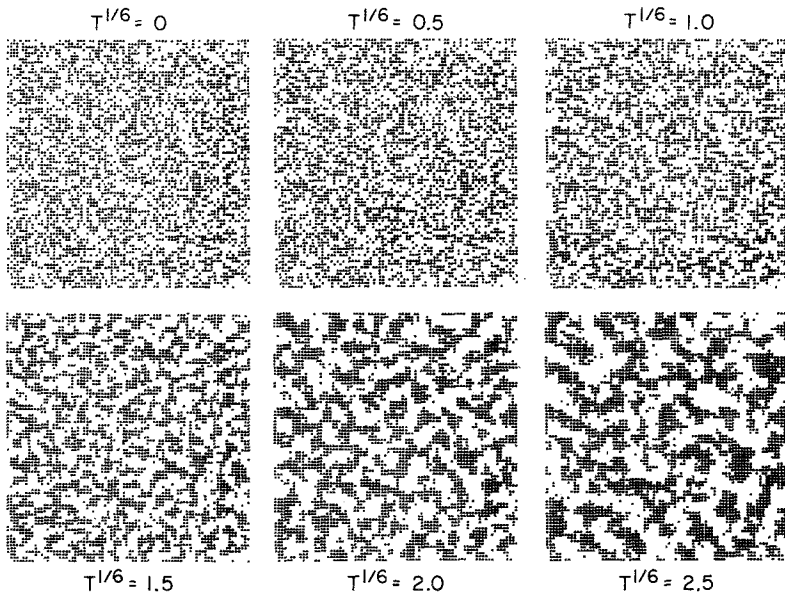


Fig. 1. Structure after annealing at various times with  $2J/kT = 0.9$ . One unit of time equals one try per site.

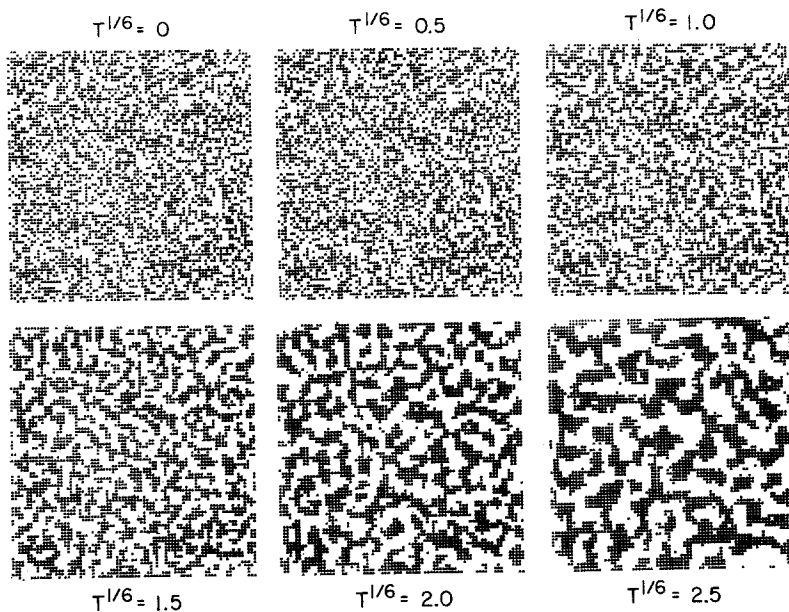


Fig. 2. Structure after annealing for various times with  $2J/kT = 1.2$ . One unit of time equals one try per site.

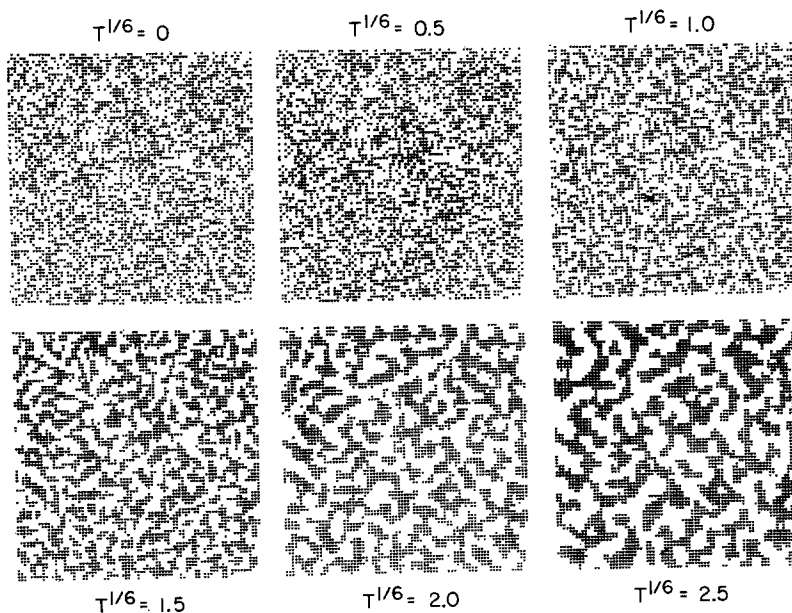


Fig. 3. Structure after annealing for various times with  $2J/kT = 1.5$ . One unit of time equals one try per site.

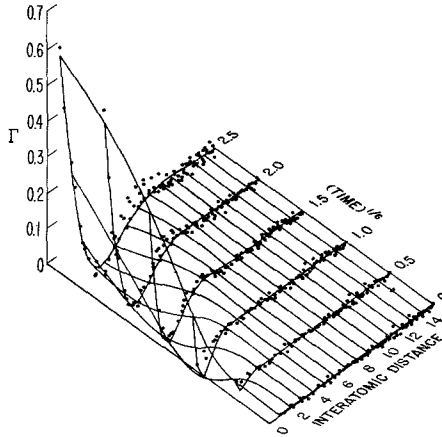


Fig. 4. Pair correlation as a function of interatomic distance and time,  $2J/kT = 0.9$ .

The pair correlation function provides a more quantitative way of presenting the kinetics of the process. The points plotted in Figs. 4–6 represent the results of the Monte Carlo calculations; the solid lines represent analytic approximations to the results.

The analytic form was based on the observation that for any time greater than zero and any temperature below the phase boundary the pair correlation

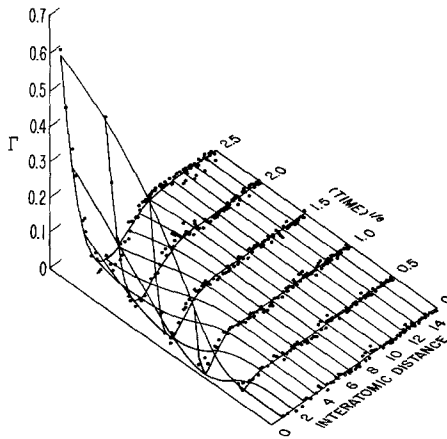


Fig. 5. Pair correlation as a function of interatomic distance and time,  $2J/kT = 1.2$ .

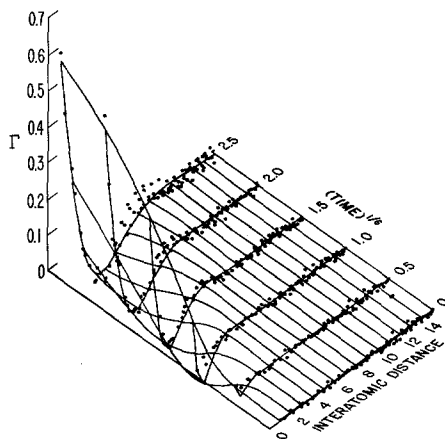


Fig. 6. Pair correlation as a function of interatomic distance and time.  $2J/kT = 1.9$ .

function depended mainly on the magnitude of  $r$  and had the form of an exponentially damped cosine function:

$$\Gamma(r) \sim e^{-sr} \cos(2\pi r/w) \quad (3)$$

with  $s \sim s_0 t^{-1/6}$  and  $w \sim w_0 t^{1/6}$ .

Some modification of these simple forms is obviously necessary to obtain sensible behavior in the limits of very short and very long times. In the very short-time limit the wavelength  $w$  cannot be allowed to become arbitrarily small; if  $w$  becomes less than four, the cosine term becomes negative for  $r = 1$ . This implies a negative correlation for nearest neighbors, which is physically absurd. This suggested the form

$$w = (a_2 t + 4^6)^{1/6} \quad (4)$$

The functional form for  $s$  must be modified to obtain proper behavior at long times as the equilibrium structure is approached. If  $s$  were allowed to increase without limit, the nearest-neighbor pair correlation would approach one, rather than the correct equilibrium value, given by<sup>(12)</sup>

$$\Gamma_m = \left( \frac{1+x}{x} \right)^{1/2} - \frac{1}{\pi} \left( \frac{1+x}{x} \right)^{1/2} \left( \frac{\pi}{2} - (1-x)K(x) \right) \quad (5)$$

where  $x = \sinh^{-2}(2J/kT)$  and  $K(x)$  is the complete elliptic integral of the first kind.

A dependence of  $s$  on  $r$  is also needed, so that the correlation does not vanish in the limit of large  $r$ . At equilibrium the composition of the two

phases is given by<sup>(13)</sup>

$$\begin{aligned} c_1 &= \frac{1}{2}[1 - (1 + z^2)^{1/4}(1 - z^2)^{-1/2}(1 - 6z^4 - z^4)^{1/8}] \\ c_2 &= \frac{1}{2}[1 + (1 + z^2)^{1/4}(1 - z^2)^{-1/2}(1 - 6z^2 + z^4)^{1/8}] \end{aligned} \quad (6)$$

where  $z = e^{-2J/kT}$ , and within one phase the correlation for very distant neighbors is

$$\Gamma_L = 4(c_1 - \frac{1}{2})^2 = 4(c_2 - \frac{1}{2})^2 \quad (7)$$

Both conditions are satisfied if  $s$  is taken of the form

$$s(r, t) = (\alpha_0 + a_1/t)^{1/6}/[1 + \gamma_0 r^6/(1 + a_3/t)]^{1/6} \quad (8)$$

where

$$\alpha_0 = [(\ln \Gamma_M)^{-6} - (\ln \Gamma_L)^{-6}]^{-1} \quad (9)$$

and

$$\gamma_0 = \{[(\ln \Gamma_L)/(\ln \Gamma_M)]^6 - 1\}^{-1} \quad (10)$$

In the limit  $t \rightarrow \infty$

$$s = \alpha_0^{1/6}(1 + \gamma_0 r^6)^{-1/6} \quad (11)$$

and for  $r = 1$

$$sr = [\alpha_0/(1 + \gamma_0)]^{1/6} = -\ln \Gamma_M \quad (12)$$

and the limit for  $r \rightarrow \infty$

$$sr \rightarrow (\alpha_0/\gamma_0)^{1/6} = -\ln \Gamma_L \quad (13)$$

A further correction should, of course, be made for the fact that the calculation was carried out for a finite system; but since at the end of the calculation the clusters were still small in comparison with the dimensions of the system, this correction was neglected.

The final functional form used for fitting the data was

$$\Gamma(r, t) = e^{-s(r,t)r} \cos[2\pi r/w(t)] \quad (14)$$

with  $s(r, t)$  and  $w(t)$  given by (8) and (4).

The values of the parameters  $a_1$ ,  $a_2$ , and  $a_3$  were determined by variable metric minimization. The numerical results for each of the temperatures studied are given in Table I, and the calculated functions are shown in Figs. 4-6.

Table I

$2J/kT$	$T/T_c$	$\Gamma_M$	$\Gamma_L$	$a_1$	$a_2$	$a_3$
0.9	0.9793	0.75652	0.56148	3.095	$4.147 \times 10^4$	$1.0 \times 10^{12}$
1.2	0.7345	0.95454	0.94791	1.810	$2.016 \times 10^4$	$1.2 \times 10^{12}$
1.5	0.5876	0.98834	0.98761	1.568	$1.212 \times 10^4$	$2.8 \times 10^{11}$

#### 4. DISCUSSION

It is apparent that the simple functional form used here is by no means perfect, but it provides a better fit than any of a variety of other simple functional forms tried, and is sufficiently good to be used for a general discussion of the process.

The wavelength parameter  $w$  is a measure of the cluster size: When the distance for which the correlation is evaluated is less than the effective cluster radius the correlation is positive; when the distance becomes greater than the cluster radius any pair at this distance is more probably unlike than like, so the pair correlation becomes negative. The first zero of the pair correlation function occurs when  $r$  equals one quarter wavelength. Thus we can regard  $w/4$  as an effective cluster radius. Phase separation begins with the smallest possible clusters, and proceeds by a coarsening process in which the clusters grow as the one-sixth power of the time.

The nearest-neighbor pair correlation is proportional to the energy change in the system; we can use it as a measure of the degree of completeness of the transformation. By this measure the process is largely complete while the clusters are still quite small, typically about five interatomic distances.

Change of annealing temperature has a definite, but not very dramatic, effect on the nature of the cluster growth. The parameter  $a_1$  decreases with decrease in annealing temperature, corresponding to greater correlation within the clusters at short distances. The parameter  $a_2$  also decreases, indicating *less rapid* coarsening at temperatures further below the critical temperature. In a physical system, of course, the "time" used here must be multiplied by the rate at which "tries" are made, which will have the usual exponential dependence on temperature of a diffusion-controlled process.

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