Time evolution of a quenched binary alloy. II. Computer simulation of a three-dimensional model system*

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We present results of the computer simulation of the time evolution of a model binary alloy following quenching. Our model system is a simple cubical lattice the sites of which are occupied either by A or B particles. There is a nearest-neighbor interaction favoring segregation into an A-rich and a B-rich phase at low temperatures, $T < T_c$. Starting from a random configuration, $T = \infty$, the system is quenched to and evolves at a temperature $(k_B\beta)^{-1}$ where the probability of an exchange between an A and B atom on nearest-neighbor sites is assumed proportional to $e^{-\beta\Delta U}(1+e^{-\beta\Delta U})^{-1}$. ΔU is the change in energy resulting from the exchange. This depends on the configuration of the ten sites neighboring the pair of sites on which the exchange would take place. In the work reported here we used a $30\times30\times30$ lattice with half the sites occupied by A particles. The system was quenched to temperatures $T/T_c = 0.6$, 0.8, 0.9, and 1.1. Results are presented for the evolution of the Fourier transform of the spherically averaged structure function $S(k,t)$ and of the energy. Comparison is made with various theories of this process and with some experiments.

I. INTRODUCTION

The phenomenon of "coarsening," which in some cases is referred to as "spinodal decomposition" (a term apparently introduced by Cahn[1]), in alloys is of great practical as well as theoretical interest. It occurs in its simplest form when an AB alloy (such as ZnAl) is quenched, i.e., cooled very rapidly from some high temperature T_0 where the system is in a molten state to a temperature $T < T_c$, the critical temperature for phase separation in the solid alloy. At temperatures below T_c the equilibrium state of the system is (for certain ranges of composition) one of coexistence of two phases, one A rich and one B rich. Since the cooling is very rapid (ideally instantaneous) there is no time for phase separation to take place and the system stays homogeneous during the quench. Consequently, the system is left in a thermodynamically unstable state and begins to undergo a process of phase segragation or coarsening. Since the alloy is now in a solid phase the motion of the atoms is hindered by potential barriers. These are overcome with the help of kinetic energy supplied by the lattice vibrations (phonons) which serve as a thermal reservoir at the quenched temperature T. The problem for the theorist is to describe the kinetics of this process which is in some ways similar (and in others different) to the development of liquid drops in a supersaturated vapor.

The classical, essentially phenomenological, theory of this process was developed by Cahn,[1] Hillert,[2] Hilliard,[3] and Cook.[4] It focuses attention on the structure function $S(\vec{k}, t)$ which is the Fourier transform of the spatial correlation function

$$G(\vec{r}, t) = \langle [\eta(\vec{r}', t) - \overline{\eta}][\eta(\vec{r}'+\vec{r}, t) - \overline{\eta}] \rangle . \qquad (1.1)$$

Here, $\overline{\eta}$ describes the average composition of the system, e.g., the fraction of A atoms less the fraction of B atoms in the whole system, and $\eta(\vec{r}, t)$ is the composition at position $\vec{r}$ at time t. The $\langle\ \rangle$ in (1.1) indicates an ensemble average (or average over $\vec{r}'$ in a macroscopic system). The function $S(\vec{k}, t)$ can, in principle and sometimes also in practice, be obtained from scattering experiments.[5]

At time $t = 0$, that is, immediately following the quench, $S(\vec{k}, t)$ is entirely structureless, since $G(\vec{r}, 0) \sim 0$ except for $\vec{r} \simeq 0$ if T_0 is sufficiently high. The classical theory predicts the existence of a certain $k_{\max}$ at which $S(\vec{k}, t)$ will have its most rapid growth during the initial stages of the coarsening process. This would correspond physically to the development of regions, whose linear dimensions are of order $2\pi/k_{\max}$ in which there is an excess of one of the phases. It is usually further assumed that during the "initial stages" of coarsening the process can be described by a linearized theory which then predicts that the peak of $S(\vec{k}, t)$ will remain at $k_{\max}$ and that S will vary exponentially with time. A Ginzburg-Landau or a linearized diffusion approach would predict that the linear size of the segregated regions grow with time[6] as $t^{1/3}$.

As we shall see later some of these predictions

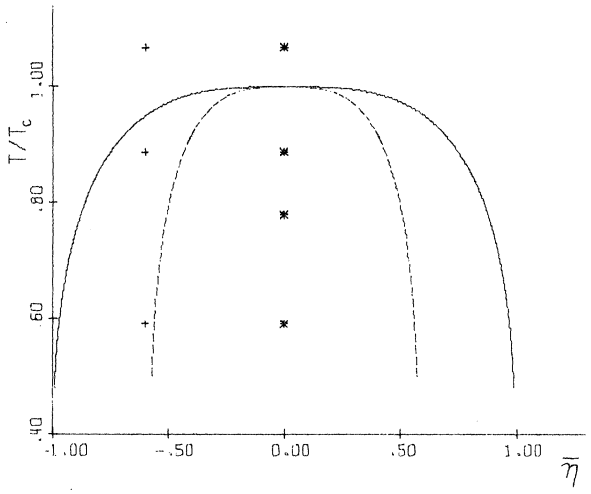

FIG. 1. Phase diagram for the AB alloy or for the infinite three-dimensional Ising model. The coexistence curve (solid line) is drawn according to a low-temperature series expansion (Ref. 12). The "spinodal" curve (dashed line), supposed boundary between metastable and unstable states, is characterized by $\partial^2 f(\bar{\eta})/\partial\bar{\eta}^2 = 0$ and is drawn assuming a free-energy density of the form $f(\eta) = -\alpha\,\eta^2 + \beta\,\eta^4$ below T_c.

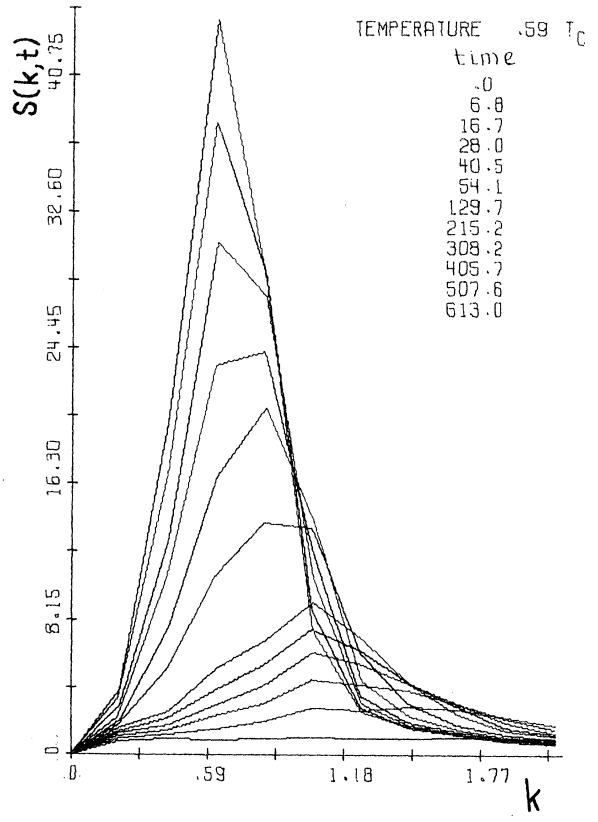

FIG. 2. Development with time of $S(k,t)$ vs k at $T = 0.59T_c$. Increasing values of the time in units of α^{-1}, Eq. (2.2), correspond to the different graphs from the bottom of the picture to the top.

do not agree with the results of our computer simulations of the process in an idealized system. Recent theoretical computations by Langer, Baron, and Miller[7] and by Binder and Stauffer[8] (which were influenced to some extent by our work) produce better agreement with these results. We shall make some detailed comparisons, especially with Langer's theory, later on. For the present, we shall content ourselves with a brief description of the general form of the kinetic equation for $S(\vec{k}, t)$ which is common to both Langer's and the classical theory. (The reader is referred to Langer's papers[6,7] for detailed discussions.) This equation can be written in the form

$$\frac{\partial S(\vec{k}, t)}{\partial t} = -2Mk^2\,[Kk^2 S(k, t) + \Omega(k, t) - k_B T]. \qquad (1.2)$$

Here, k_B is Boltzmann's constant, M is a positive "mobility constant;" K, also a positive constant, is the coefficient of the gradient term in the expression for the "coarse-grained" free-energy functional

$$F(\{\eta\}) = \int [f(\eta) + \tfrac{1}{2}K(\vec{\nabla}\eta)^2]\,d\vec{r}\,. \qquad (1.3)$$

This free energy is assumed, both in the classical

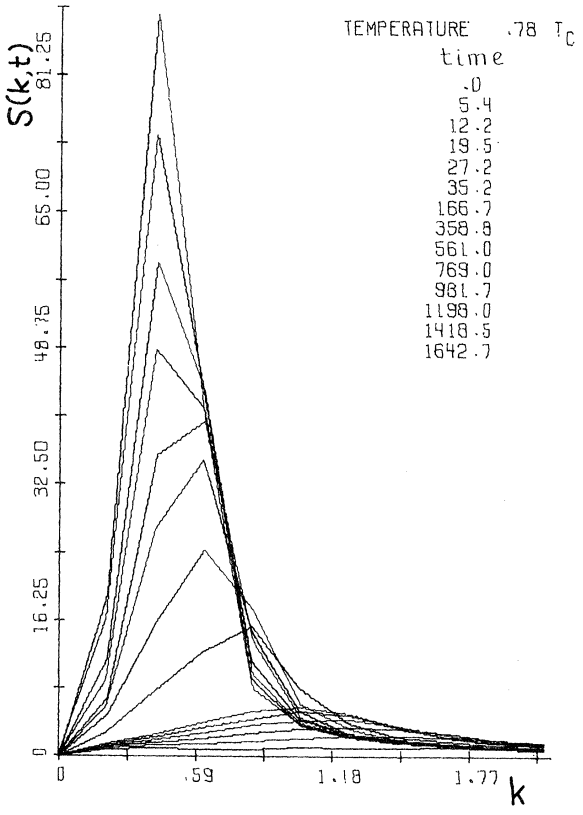

FIG. 3. Development with time of $S(k,t)$ vs k at $T = 0.78T_c$.

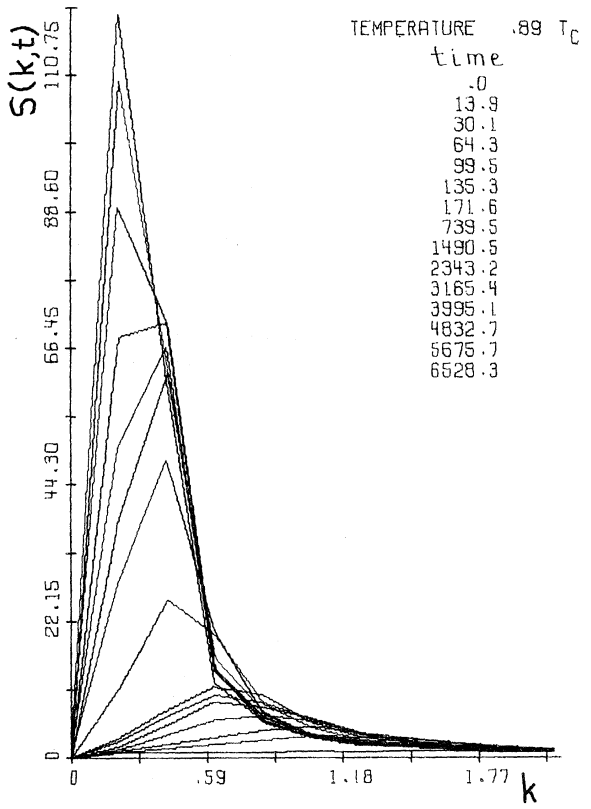

FIG. 4. Development with time of $S(k,t)$ vs k at $T = 0.89T_c$.

theory[1] and in Langer's semimicroscopic theory, to describe the quenched (nonequilibrium) system with a spatial composition $\eta(\vec{r}, t)$. In particular, the gradient of the variational derivative of F with respect to $\eta(\vec{r}, t)$, which is interpreted as the local chemical potential, furnishes the driving force for spinodal decomposition. The term $\Omega(\vec{k}, t)$ on the right side of (1.2) depends on $f(\eta)$ and is very complicated; indeed according to theory[1,7] it should not be expressible in terms of $S(\vec{k}, t)$ so that (1.2) would not be a closed equation. It is therefore necessary to approximate it in some way and it is the manner in which this term is approximated that distinguishes the different theories for all practical purposes. In the linearized classical theory $\Omega(\vec{k}, t)$ is set equal to $[\partial^2 f(\bar{\eta})/\partial\bar{\eta}^2]S(\vec{k}, t)$, while in the theory developed by Langer, Bar-on, and Miller[7] $\Omega(\vec{k}, t)$ is assumed to be of the form $A(t)S(\vec{k}, t)$, where $A(t)$ depends both on $f(\eta)$ and on $S(\vec{k}, t)$ in a highly nonlinear way (but is independent of k).

It is the purpose of the computer simulation work reported here to obtain explicitly the time behavior of $S(\vec{k}, t)$ and other quantities of interest for a simple model system. We believe that despite the many crude oversimplifications of reality made in our model (which is described in Sec. II) it contains the essential physical features of the processes occurring in real systems after quenching; indeed we obtain results which are very similar to experimental results, cf. Sec. V. If this is granted, then it follows that any theory claiming to describe this process in real physical systems should also be able to describe in a quantitative way what happens in our model system. The model is thus useful as a test of theory. Even more important, the model, because of its flexibility can be used in some cases to identify the important physical steps in the coarsening process which need to be built into a good theory.

II. DESCRIPTION OF MODEL

The model system we are using here is the same as that used by Bortz *et al.*[9] to simulate this process in two dimensions. (We refer the reader to that paper, to be called I, for details, see also Flinn[10] and Binder.[11]) At each site of a simple cubic lattice there is assumed to be either an A atom or a B atom. We let $\eta(\vec{r}_i) = +1$ (-1) when there is an A (B) atom at the site $\vec{r}_i$. The $\vec{r}_i$ range over an $L \times L \times L$ cubical region containing $L^3 = N$ sites (the lattice constant is unity). This system

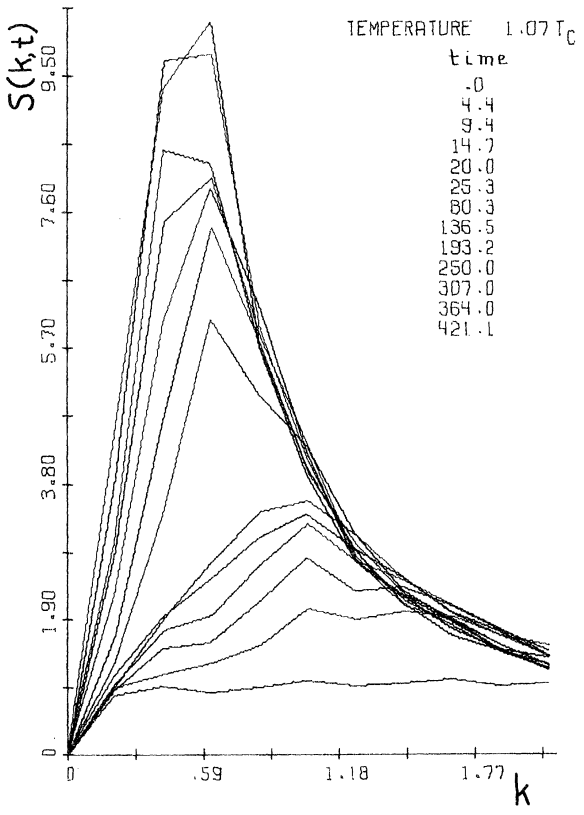

FIG. 5. Development with time of $S(k,t)$ vs k at $T = 1.07T_c$.

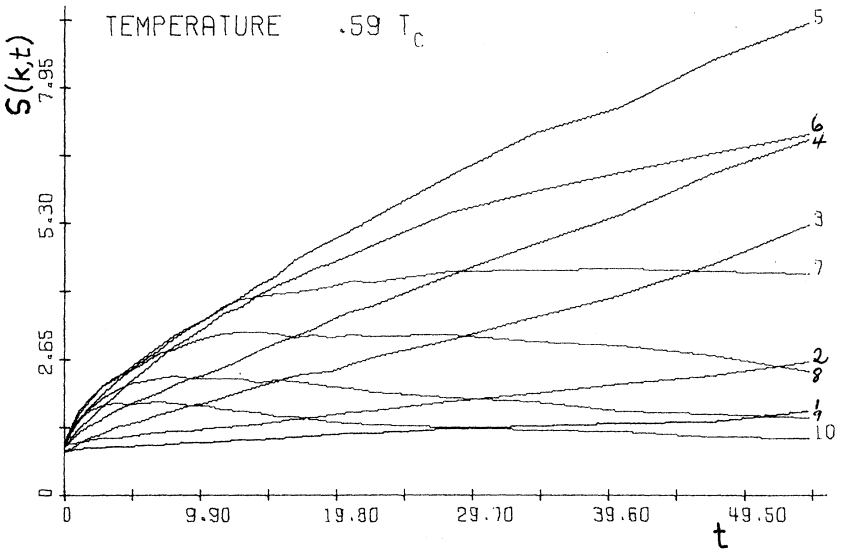

FIG. 6. Early-time evolution of $S(k,t)$ as a function of time for different values of k at $T = 0.59T_c$. At the end of each line is shown the corresponding value of $\mu = 30k/2\pi$.

is isomorphic to an Ising-spin system where the spin at each site can point "up or down" and to a lattice gas where each site can be either occupied or empty.

We assume an interaction between atoms on nearest-neighbor sites of the form

$$U = J \sum{}' \eta(\vec{r}_i)\eta(\vec{r}_j) . \qquad (2.1)$$

The sum in (2.1) is over nearest-neighbor sites and we use periodic (toroidal) boundary conditions so that corresponding atoms on opposite faces are considered nearest neighbors. For $J > 0$, the situation considered here, the low-temperature equilibrium state of this system is one in which there is a segregation into A-rich and B-rich phases. [This corresponds to regions with up and down magnetization in the Ising-spin language. We are also carrying out computations for $J < 0$, in which case the equilibrium state below T_c is for a certain range of η an "ordered" (antiferromagnetic) one.]

The phase diagram of this system, in the thermodynamic limit $L \to \infty$, is shown in Fig. 1, using low-temperature Padé approximants and a $\frac{5}{16}$ power law near $T_c \simeq 4.510 J/k_B$.[12]

The kinetics of our model are described, as in I, by specifying the probability per unit time for an interchange of an A and B atom located on *nearest-neighbor sites* $\vec{r}_i$ and $\vec{r}_j$. We set this equal to

$$P_{ij} = \alpha e^{-\beta \Delta U_{ij}}/(1 + e^{-\beta \Delta U_{ij}}) , \qquad (2.2)$$

where $\beta = (k_B T)^{-1}$ and ΔU_{ij} is the change in the energy of the system which would result from the in-

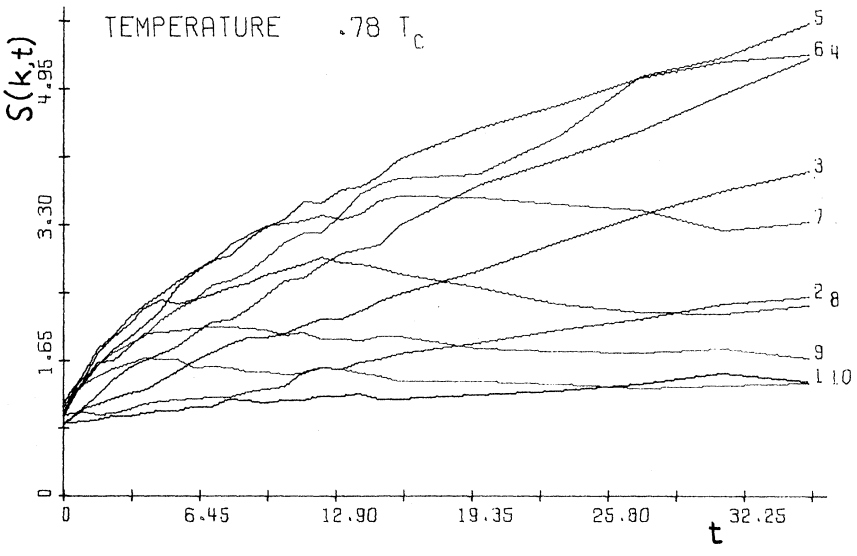

FIG. 7. Early-time evolution of $S(k,t)$ as a function of time for different values of k at $T = 0.78T_c$.

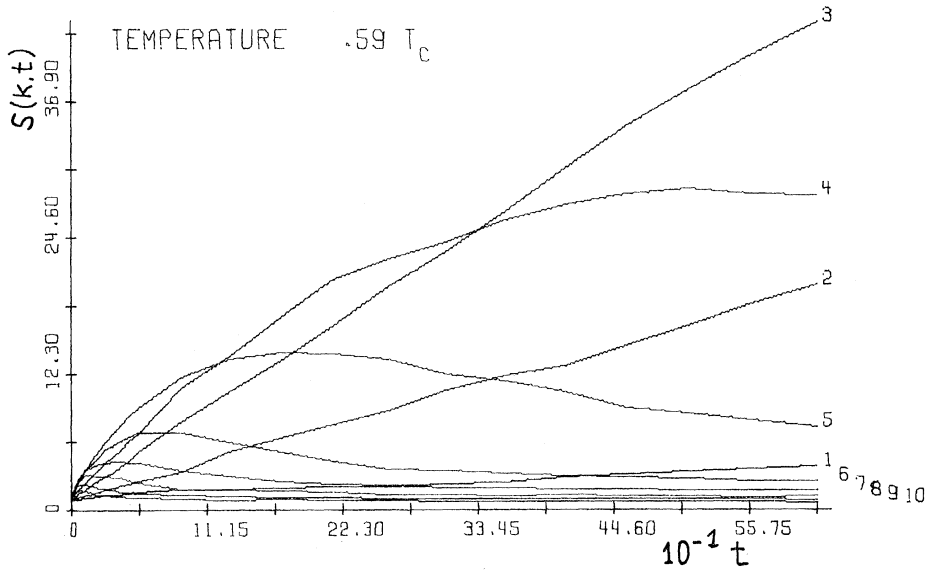

FIG. 8. Complete evolution with time of the spherical averaged structure function for different values of k at $T=0.59T_c$.

terchange. This change depends on the configuration of atoms on the ten sites surrounding the pair $\vec{r}_i$, $\vec{r}_j$. α^{-1} is taken to determine the unit of time and treated as if it were independent of the configuration of the neighbors and of the temperature. (In comparisons with experiments on real systems α will certainly need to be taken temperature dependent since the strength of the phonon reservoirs decrease with temperature. This amounts however only to a change in the time scale, cf. Sec. V.)

To carry out the computer simulation we start the system with N_A (N_B) particles of type A (B) in a completely random configuration, i.e., N_A sites are picked at random from the available N sites and designated as the position of the A atoms. We then follow the time evolution of the system as exchanges take place between unlike atoms on neighboring sites according to the Markov transition probability (2.1) (see also Bortz, Kalos, and Lebowitz[13]). The expected value of any function of the configuration at time t can be obtained by taking the average over many independent runs. (We expect however that for functions which are extensive, like the energy and a smoothed S, the number of runs needed should decrease with the size of the system; for a macroscopic size system almost every run should produce typical results.) In the work reported here $L=30$, $N=27\,000$, and the number of runs was eight.

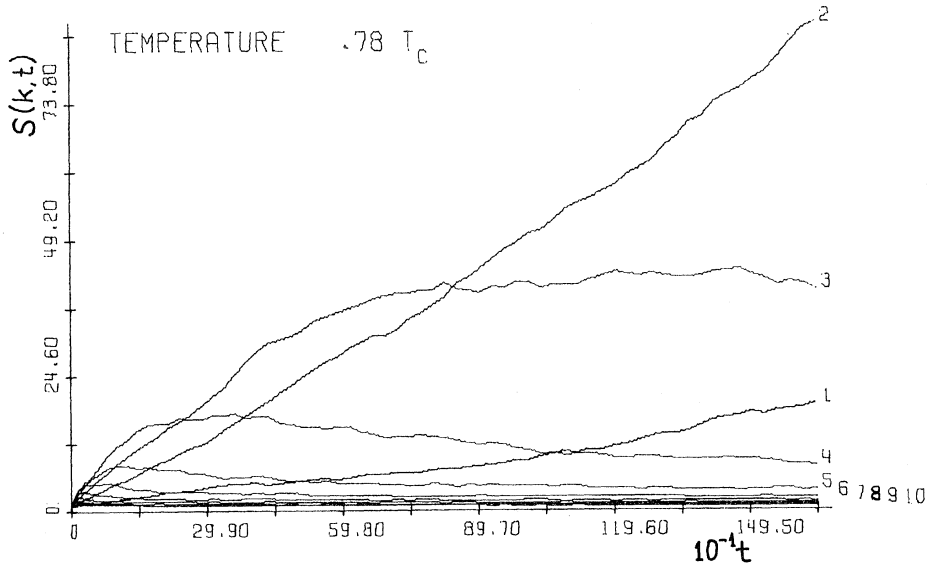

FIG. 9. Complete evolution with time of the spherical averaged structure function for different values of k at $T=0.78T_c$.

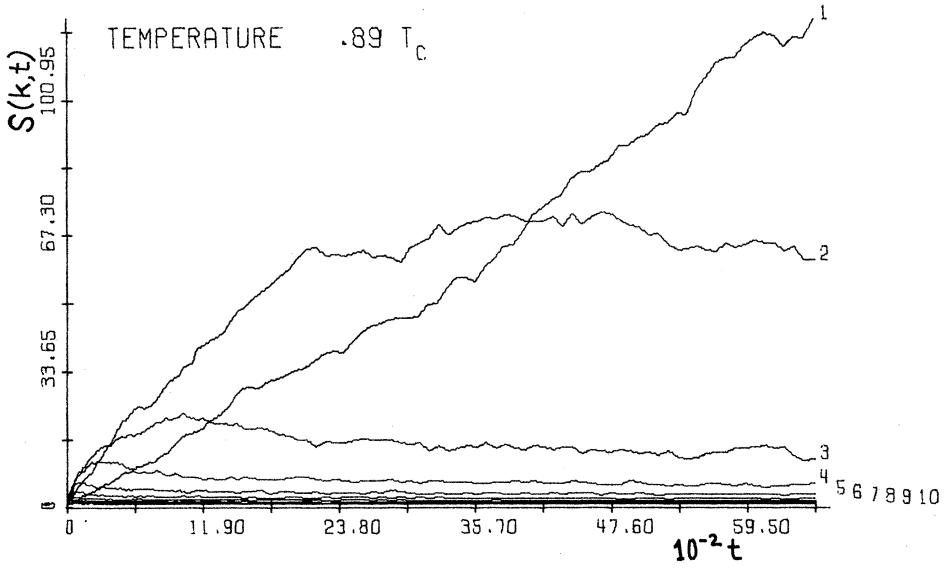

FIG. 10. Complete evolution with time of the spherical averaged structure function for different values of k at $T = 0.89 T_c$.

A. Computation of system properties

For this system (see I),

$$S(\vec{k}, t) = \sum_{\vec{r}} e^{i\vec{k}\cdot\vec{r}} G(\vec{r}, t) , \tag{2.3}$$

$$G(\vec{r}, t) \equiv N^{-1} \sum_{\vec{r}_i} [\eta(\vec{r}_i + \vec{r}, t)\eta(\vec{r}_i, t) - \bar{\eta}^2] , \tag{2.4}$$

where $\vec{r}$ and $\vec{r}_i$ run over the $N = 27\,000$ sites,

$$\bar{\eta} = N^{-1} \sum \eta(\vec{r}) = N^{-1}(N_A - N_B) ,$$
$$\vec{k} = (\tfrac{2}{30}\pi)\vec{\mu} = (\tfrac{2}{30}\pi)(\mu_x, \mu_y, \mu_z) , \tag{2.5}$$

with

$$\mu_\alpha = 0, 1, \ldots, 29, \quad \alpha = x, y, z$$

and we have indicated explicitly in (2.4) the time dependence of $\eta(\vec{r}_i)$. Note that from our definition,

$$N^{-1} \sum_{\vec{k}} S(\vec{k}, t) = 1 - \eta^{-2} , \tag{2.6}$$

$$S(\vec{k} = 0, t) = 0 , \tag{2.7}$$

and that corresponding to the random initial configuration present at $t = 0$, immediately following quenching,

$$S(\vec{k}, 0) \simeq 1 - \bar{\eta}^2 \text{ for } \vec{k} \neq 0 . \tag{2.8}$$

The energy U, given by (2.1), is related simply to the value of $G(\vec{r}, t)$ for $\vec{r}$ a nearest-neighbor vector. If we denote this value of G (averaged over the three orientations) by $\frac{1}{3} g$, we have

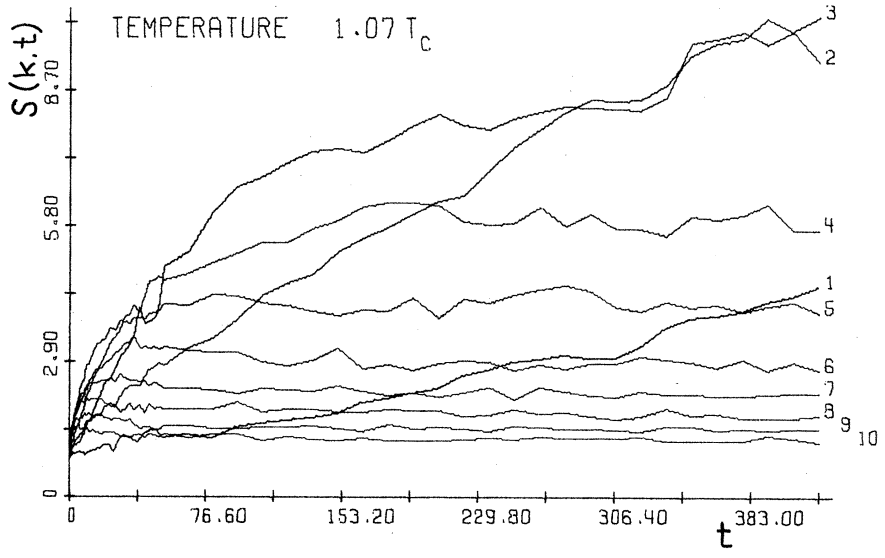

FIG. 11. Complete evolution with time of the spherical averaged structure function for different values of k at $T = 1.07 T_c$.

$$U/N = -3J(g+\eta^{-2}) = J(2N_{AB}/N - 3) = (2u-3)J\ , \quad (2.9)$$

where N_{AB} is the number of A-B bonds and $u = N_{AB}/N$.

We also define the spherical averaged structure function

$$S(k,t) = \sum_{\vec{k}}{}' S(\vec{k},t) \Big/ \sum_{\vec{k}}{}' 1\ , \quad (2.10)$$

where $k = \frac{2}{30}\pi\mu$, $\mu = 1, 2\cdots$, and the sum $\sum_{\vec{k}}'$ goes over all values of $\vec{k}$ such that $\frac{2}{30}\pi\mu \le |\vec{k}| < \frac{2}{30}\pi(\mu+1)$. In the actual simulation we computed $S(\vec{k},t)$ for $\vec{k}$ in one octant of the reciprocal lattice up to $|\vec{k}| = \frac{2}{3}\pi$, i.e., in ten shells. The number of $\vec{k}$ values in the different shells are 6, 13, 19, 39, 55, 72, 91, 114, 169, 178.

III. RESULTS

We report here the results of our observations of the time evolution of $S(k,t)$ and the energy U after quenching our system to temperatures $T/T_c = 0.59$, 0.78, 0.89, and 1.07. $N_A = N_B = 13\,500$, $\bar{\eta} = 0$. (We have also carried out computations, at these temperatures, for $N_A = 0.2N$; these will be reported separately.) The three lower temperatures are in the two-phase region of the phase diagram, the "spinodal" region, while $T = 1.1\,T_c$ is in the one-phase region, see Fig. 1. This latter temperature is however sufficiently close to T_c that significant "local ordering" may be expected which for short times might look very similar to coarsening. All our results are averages over eight independent runs which appeared sufficient to wash out most fluctuations. The estimated reliability (essentially the rms fluctuation) is indicated in some of the figures. The data were collected at initially assigned intervals of a certain number of (actual) exchanges. The intervals were increased as time progressed and the evolution slowed down.

The spherically averaged structure function $S(k,t)$ is plotted in Figs. 2–5 as a function of k for different values of t after quenching to the temperatures mentioned earlier. The growth of the peak and its shift to smaller values of k are evident and are similar to what is observed experimentally.[5] In Figs. 6–11, $S(k,t)$ is plotted as a function of time for different values of k, Figs. 6 and 7 corresponding to the very early time behavior at two temperatures which are representative of all temperatures studied.

It is clear from these figures that there is no time regime in which $S(k,t)$ can be said to grow exponentially with time. As in our two-dimensional study, reported in I, $S(k,t)$ for each value of k has an initial growth in time, reaches a peak, and decays. The time required to reach the peak increases as k decreases and the peak is never reached, during the course of the experiment, for the smallest values of k. The slope of $S(k,t)$ vs t appears to decrease monotonically with t (for almost all values of k) until $S(k,t)$ is past its peak. As the temperature is increased, the decay after the peak is reached becomes less pronounced and for $T = 1.1\,T_c$, $S(k,t)$ appears to reach its maximum value for each k, beginning with the largest values of k, and remains there. This agrees with some predictions of Langer[6] and is similar to what happened in the two-dimensional case.

The behavior of u defined in (2.9) with time was also studied. At $t = 0$, the number of A-B bonds is approximately $\frac{1}{2}3N$ so $u = \frac{3}{2}$. After a rapid initial decrease u appears to behave as $(t+10)^{-b}$: This behavior must clearly be modified for still longer times when u should approach a finite value $u_\infty(T)$, which will be very small at low temperatures.

Unfortunately, we have no reliable way of estimating $u_\infty(T)$, the equilibrium value of u for our system at $T < T_c$. What exists in the literature[14,15] are estimates based on Padé approximants for the equilibrium energy in the pure phase $u_p(T)$, i.e., along the coexistence line and in the one-phase region $\bar{\eta} = 0$ for $T \ge T_c$. The size-effect corrections to this energy can be expected to be very small for our system.[15] What is not negligible for our system are the interfacial energies, which since we have a *finite* system (with a fixed value of $\bar{\eta}$) give a nonvanishing $u_\infty(T)$ even for $T = 0$, $u_\infty(0) = \frac{1}{15}$, $\bar{\eta} = 0$. Fisher[16] suggested that we estimate this interfacial energy $u_I(T)$, for $T < T_c$, by multiplying $u_I(0)$ by the surface tension $\sigma(T)$. This would give

$$u_\infty(T) \simeq u_I(0)\,\sigma(T) + u_p(T)\ , \quad (3.1)$$

where $\sigma(T) = 0$ and $u_p(T)$ is the one-phase equilibrium u for $T \ge T_c$ and $\sigma(0) = 1$, $u_p(0) = 0$. Using for $\sigma(T)$ the results of Monte Carlo computations[17] we have analyzed the variation of $u - u_\infty(T)$ with time, assuming an asymptotic behavior of the form

$$u - u_\infty(T) \sim t^{-b'}\ .$$

We have also looked, in a similar way, at the behavior of $u - u_p(T)$,

$$u - u_p(T) \sim (t+10)^{-b''}\ .$$

TABLE I. Values of b, b', and b'' obtained from a mean-square fit to the data from $t \ge 50$. The corresponding rms fluctuations for increasing temperatures are 1.6, 2.7, 2.7, and 1.6%; 1.1, 2.1, 4.2, and 12.7%; 1.2, 2.3, 4.0, and 11.9%, respectively.

T/T_c	b	b'	b''
0.6	0.16	0.22	0.18
0.8	0.10	0.22	0.16
0.9	0.06	0.21	0.13
1.1	0.02	0.79	0.79

The values of b, b', and b'' at different temperatures are listed in Table I.

For the two-dimensional case we reported in I, $b(\sim b'') \sim \frac{1}{5}$ at $T = 0.58T_c$ and $b' \sim \frac{7}{12}$ for $T = 1.1T_c$; the only two temperatures analyzed there. [The computations reported in I have been extended to longer times and now appear to give $b \sim \frac{1}{4}$ at $0.58T_c$; Rao, Marro, Kalos, and Lebowitz (unpublished).]

The behavior of b at the lowest temperatures is in good accord with a prediction of Binder and Stauffer[8] which gives, at "low temperatures" $b'' = (d+3)^{-1}$, d the dimensionality of the space considered. For $T > T_c$, on the other hand, these authors predict $b' \simeq \frac{1}{2}d$, but there may be a crossover effect for $T \simeq T_c$.[18] It is not clear to us at the present time how much weight one should put on the fits or misfits between our results and the predictions. Our data is *limited* (as is clear from Table I) and the theory may or may not be adequate.

The number of (actual) exchanges versus time was also studied. We expect the number of exchanges per unit time should behave, at the lower temperatures, approximately like the number of A-B bonds. This was confirmed by our results which gave for the slope of a log-log plot, at increasing temperatures, 0.86, 0.94, 0.97, and 1.05, respectively. (It is not exactly the same since the probability of an exchange depends on the configuration on the sites surrounding the A-B pair. When the A and B regions are segregated, however, this should affect the rate only through a constant factor.)

Two important parameters characterizing the time evolution of $S(k, t)$ are the location of the peak, $k_m(t)$ and the height of the peak $S(k_m(t), t)$. Due to the finite (small) size of our system, which leads to a wide spacing between the values of k we can measure, it is difficult to determine these parameters precisely. Under a parabolic fit to three values of k around k_m we find a reasonable fit with the following formulas:

$$k_m(t) \simeq \alpha'(t+10)^{-a'}, \tag{3.2}$$

$$S(k_m(t), t) \simeq \alpha''(t+10)^{a''}. \tag{3.3}$$

TABLE II. Values of a, a' and a''. The corresponding rms fluctuations for increasing temperatures are approximately 1.6, 2.7, 7.4, and 5.8%; 3.7, 6.4, 6.4, and 4.8%; and 0.5, 1.1, 2.1, and 1.1%; respectively.

T/T_c	a'	a''	a
0.6	0.21	0.69	0.17
0.8	0.25	0.74	0.21
0.9	0.25	0.65	0.23
1.1	0.22	0.38	0.12

We also computed $\bar{k}(t)$, the first moment of $S(k, t)$. $\bar{k}(t)$ which behaves more smoothly than $k_m(t)$ and its "asymptotic" behavior is well described by

$$\bar{k}(t) \sim \alpha(t+10)^{-a}. \tag{3.4}$$

The values of a, a', and a'' are listed in Table II.

Binder and Stauffer's[8] predictions are for $a'' = 3a'$ and $a' = b' = \frac{1}{6}$ at "low temperatures." The first of these predictions seems to be well satisfied for $T = 0.6T_c$ and $T = 0.8T_c$, the second apparently not. For $T \simeq T_c$, they predict $a' \simeq \frac{1}{4}$ and for $T > T_c$, $a' = \frac{1}{2}$. Only the first of these predictions seems in agreement with our results, but again we may be too close to T_c[18]. The results of Ref. 7 are consistent[19] with $a' \sim 0.21$.

We have also investigated the shape of $S(k, t)$ for $k > k_m$ by fitting it to the formula

$$S(k, t) = c_1(t)/[k^2 + c_2(t)]. \tag{3.5}$$

For $T = 1.1T_c$, c_1 and c_2 become time independent very early, while for low temperatures the c's definitely change with time. We also find that $c_2 < 0$ for $T/T_c = 0.6$ and 0.8 as one would expect for $T < T_c$.[6]

IV. COMPARISON WITH LANGER'S THEORY

As indicated in Sec. I the different theories of spinodal decomposition all make use of the free-energy expression (1.3). Both the classical theory and the one worked out by Langer *et al.*[7] approximate $f(\eta)$ by an even quartic polynomial [in our model there is a rigorous symmetry about $\bar{\eta} = 0$ (cf. Cahn[14])]. *Assuming* the validity of dynamical scaling, the function $S(k, t)$ may be expressed in the vicinity of the critical temperature $T \lesssim T_c$ in a "universal form" $s(q, \tau)$ in terms of the dimensionless variables[7]

$$\tau = \alpha_1(1 - T/T_c)^{\gamma+2\nu}t, \quad q = \alpha_2(1 - T/T_c)^{-\nu}k, \tag{4.1}$$

$$s(q, \tau) = \alpha_3(1 - T/T_c)^{\gamma}S(k, t). \tag{4.2}$$

The values of the parameters for the kinetic three-dimensional Ising model simulated here are given in Ref. 7 as

$$\gamma = \tfrac{5}{4}, \quad \nu = \tfrac{9}{14}, \quad \alpha_1 = 3.51, \quad \alpha_2 = 0.35, \quad \text{and} \quad \alpha_3 = 2.59.$$

In Fig. 12 we plot $s(q, \tau)$ as a function of τ for selected values of q. If scaling is valid and we were in the region of scaling (which we definitely are not for $T = 0.6T_c$ and only marginally for $T = 0.8T_c$) then, for a given q, $s(q, \tau)$ should be the same function of τ for different temperatures. Surprisingly enough, for $q \simeq 1$ this is the case even for $T = 0.6T_c$. For smaller values of q the deviations increase as τ increases. (It is because of the scaling of t that we ran our computer simulations to larger values of t for T closer to T_c.)

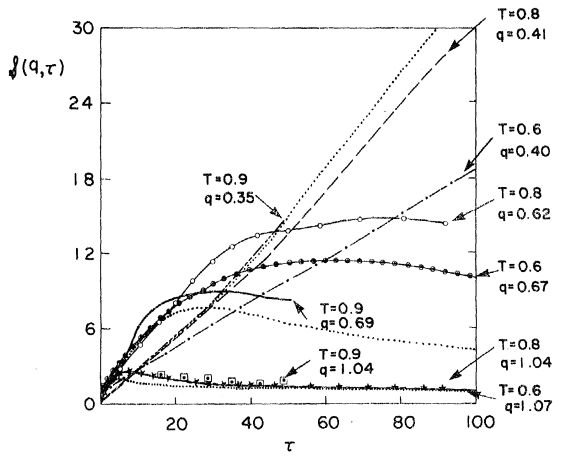

FIG. 12. Structure function vs time in reduced units for three different values of q (scaled k) and different temperatures. Note that for $q \simeq 0.65$ (which is in the neighborhood of the peak of $S(q, \tau)$ for intermediate times, see Figs. 13 and 14) the results for $T = 0.9T_c$ can be affected by the slight differences between the chosen values of q. The dotted lines correspond to Langer's predictions for similar values of q.

In terms of the reduced variables q and τ, the approximation by Langer *et al.* for $\Omega(k, t)$ in (1.2), $\Omega(k, t) = A(t)\, S(k, t)$ leads to the equation

$$\frac{\partial S(q, \tau)}{\partial \tau} = -q^2[q^2 + a(\tau)]S(q, \tau) + q^2 . \qquad (4.3)$$

It was this equation which was solved in Ref. 7 and the results compared in part with our computer simulation. We make such a comparison in Figs. 13 and 14 where we compare the function $S(q, \tau)$ obtained by Langer *et al.* from the solution of (4.3) (and an equation for A) with the results of our simulation. The agreement for $T = 0.8T_c$ and $0.9T_c$ is quite impressive. As a more direct, and more stringent, test of the approximation (4.3) we have also plotted in Fig. 15 the function

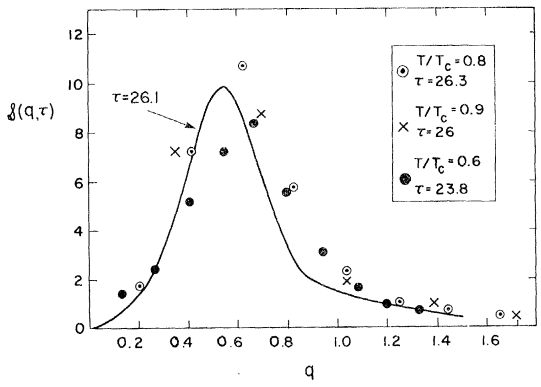

FIG. 13. Comparison of the computer simulation results with those of Ref. 7 (solid curves) for $\tau \simeq 26$.

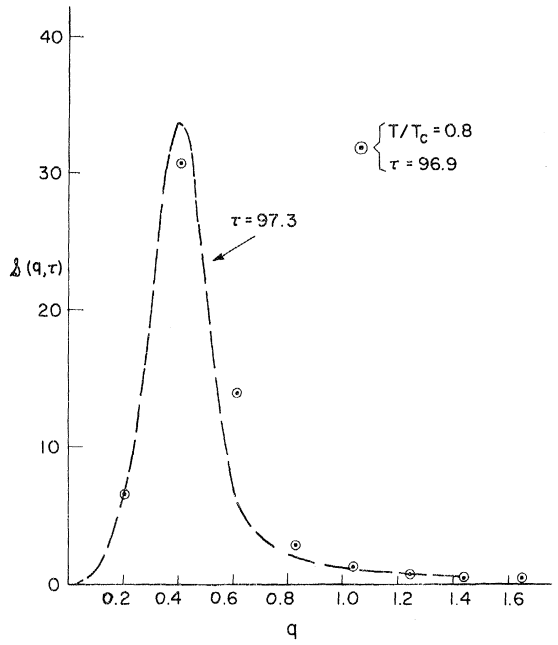

FIG. 14. Comparison of the computer simulation results with those of Ref. 7 (solid curves) for $\tau \simeq 97$.

$$\Gamma(q, \tau) \equiv \left(\frac{1}{q^2}\frac{\partial S(q, \tau)}{\partial \tau} - 1\right) S^{-1}(q, \tau) + q^2 , \qquad (4.4)$$

which is taken directly from our computer simulation. According to (4.3), $\Gamma(q, \tau)$ should be independent of q and of the temperature T if $T \lesssim T_c$.

Finally, in Figs. 16 and 17 we plot the function $R(q, \tau)/q^2$, where R is the logarithmic derivative of S,

$$R(q, \tau) \equiv \frac{\partial}{\partial \tau} \ln S(q, \tau) \qquad (4.5)$$

This is a quantity usually plotted by experimentalists,[5] and our results are in qualitative agreement with those obtained experimentally. The linear classical theory would predict a straight line, in disagreement with experiment.

V. COMPARISON WITH EXPERIMENT

In order to compare the results of the computer simulation with possible real experiments on idealized systems (i.e., being able to neglect vacancies, defects, etc.), we have to establish some (order-of-magnitude) relation between our units of length and time and those of real systems. Our unit of length is clearly the lattice spacing a_0, which is of the order of several angstroms; in the experiments of Rundman and Hilliard[5(b),5(c),20] on aluminun-zinc alloy (22-at.% Zn) at $423°\,\mathrm{K} \simeq 0.7T_c$, $a_0 \sim 2.5$ Å. Thus, our $k = 2\pi\mu/30a_0 \sim 0.84\mu \times 10^7/\mathrm{cm}$; the location of the peak in the Rundman-Hilliard experiment was around $k \lesssim 10^7/\mathrm{cm}$. Interest-

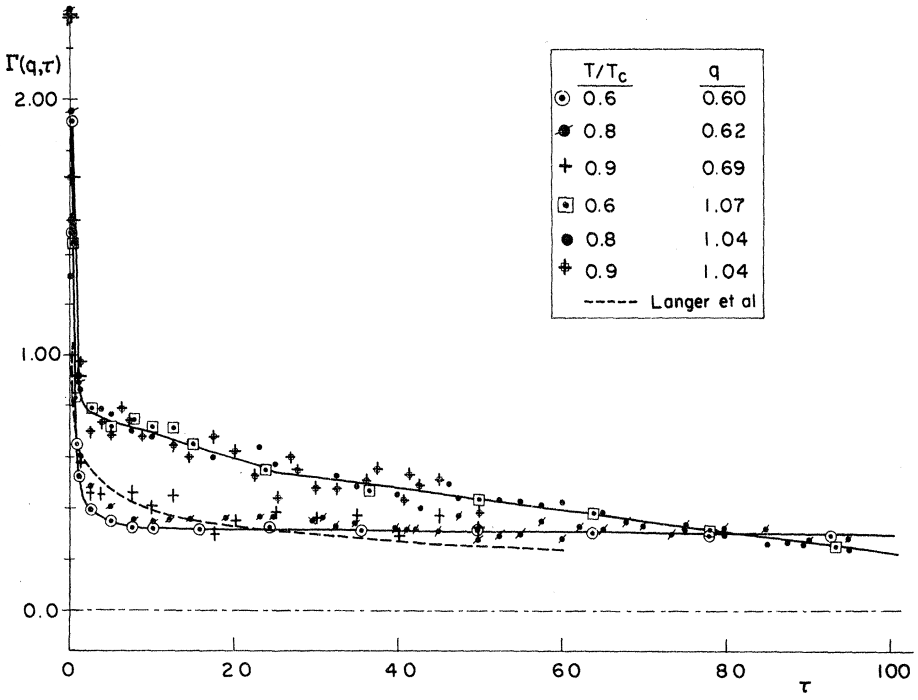

FIG. 15. Time evolution of the function $\Gamma(q,t)$ as defined in Eq. (4.4). The dashed line is obtained using the approximation made in Ref. 7.

ingly enough, the location and height of the peak in these experiments appears to behave with time in accordance with Eqs. (3.2) and (3.3) with $a' \simeq 0.2$ and $a'' \simeq 0.7$, which are close to the values found by us. Our unit of time is α^{-1} which according to (2.2) is just one-half of the average time between exchanges which do not change the energy of a configuration, e.g., $2/\alpha$ is the mean time between jumps to a neighboring site for an A atom in a sea of B atoms. Hence, according to (2.2), α^{-1} is related simply to the diffusion coefficient of an A atom in a crystal of B atoms (and *vice versa*),

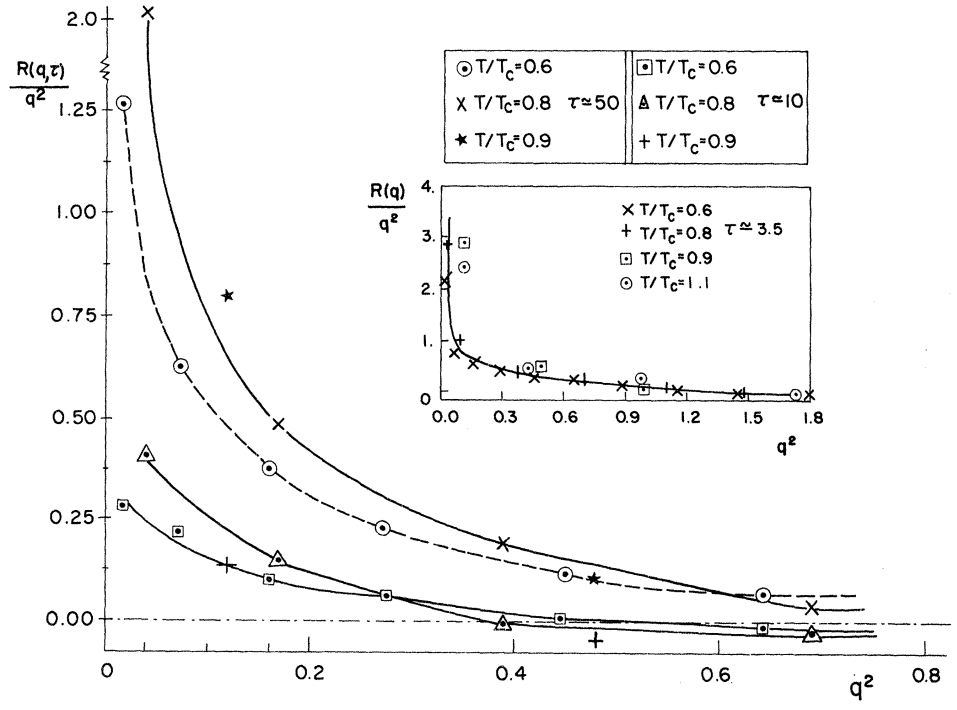

FIG. 16. Function $R(q,t)/q^2$ [see Eq. (4.5)] vs q^2 for different times (reduced units). The inset corresponds to earlier times. There is only little temperature dependence but a definite time dependence, that has also been reported in scattering experiments (Ref. 5).

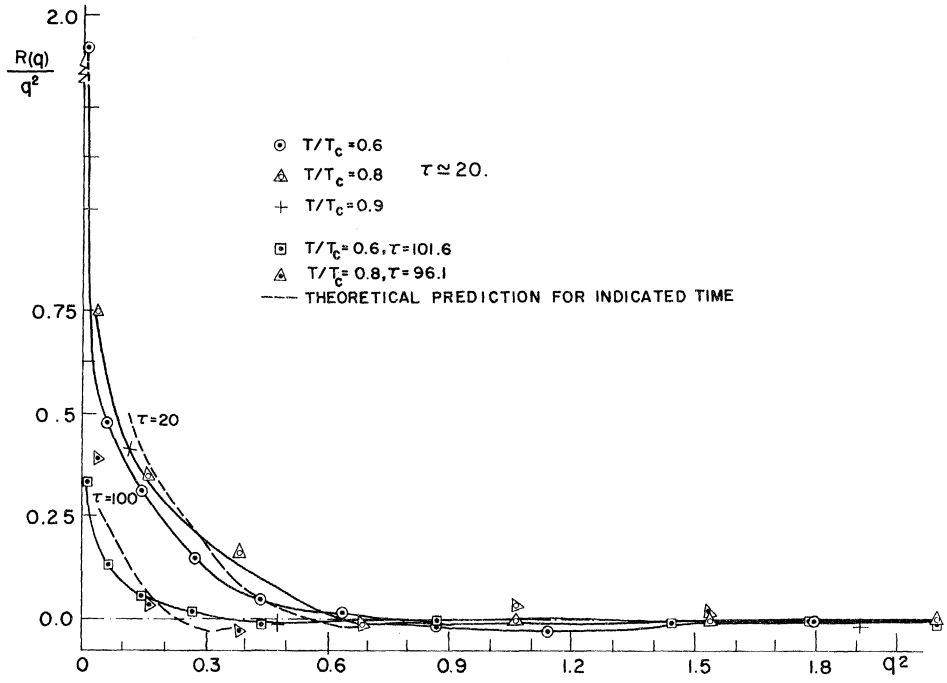

FIG. 17. Same plot as in Fig. 16 for $\tau \simeq 20$ and $\tau \simeq 100$ including the comparison with the calculations by Langer *et al.* (Ref. 7).

$$\alpha^{-1}(T) = a_0^2/[12D_0(T)],$$

where $D_0(T)$ is the diffusion constant at temperature T in the limit of zero concentration of A (B) atoms (when the system would of course be in a one phase). If we set[4,20,21] $D_0(T) \sim 10^{-15}$ cm^2/sec for the Rundman-Hilliard experiment, then $\alpha^{-1} \sim \frac{1}{20}$ sec.

We should mention here that we have been recently informed by Goldburg and Huang[22] that in their experiments on a binary fluid,[23] which is quenched into the two-phase region *very* close to T_c, they find that $S(k_m(t), t)$ does initially grow exponentially with t (as would be predicted by a linearized theory). The exponent appears to depend very strongly on $T - T_c$.

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[1]J. W. Cahn, Acta Metall. 9, 795 (1961); 10, 179 (1962); see also Trans. Metall. Soc. AIME 242, 166 (1968).

[2]M. Hillert, Acta Metall. 9, 525 (1961).

[3]J. E. Hillard, in *Phase Transformations*, edited by H. I. Aaronson (American Society for Metals, Metals Park, Ohio, 1970).

[4]H. E. Cook, Acta Metall. 18, 297 (1970).

[5](a) M. Hillert, M. Cohen, and B. L. Averbach, Acta Metall. 9, 536 (1961); (b) K. B. Rundman and J. E. Hilliard, *ibid.* 15, 1025 (1967); (c) K. B. Rundman, Ph.D. thesis (Northwestern University, 1970); (d) E. P. Butler and G. Thomas, Acta Metall. 18, 347 (1970); (e) G. F. Neilsen, Phys. Chem. Glasses 10, 54 (1969); (f) N. S. Andrew, G. G. Boiko, and N. A. Bokov, J. Non-Cryst. Solids 5, 41 (1970); (g) M. Tomazawa, R. K. Mac Crone, and H. Herman, J. Amer. Ceram. Soc. 53, 62 (1970).

[6]J. S. Langer, Ann. Phys. (N.Y.) 65, 53 (1971); Acta Metall. 21, 1649 (1973); Physica (Utr.) 73, 61 (1974); J. S. Langer and M. Bar-on, Ann. Phys. (N.Y.) 78, 421 (1973); I. M. Lifshitz and V. V. Slyozov, J. Phys. Chem. Solids 19, 35 (1961).

[7]J. S. Langer, M. Bar-on, and H. D. Miller, Phys. Rev. B 11, 1417 (1975).

[8]K. Binder and D. Stauffer, Phys. Rev. Lett. 33, 1006 (1974); also K. Binder (private communication).

[9]A. B. Bortz, M. Kalos, J. Lebowitz, and M. Zendejas, Phys. Rev. B 10, 535 (1974).

[10]P. A. Flinn, J. Stat. Phys. 10, 89 (1974).

[11]K. Binder, Z. Phys. 267, 213 (1974).

[12]J. W. Essam and M. Fisher, J. Chem. Phys. 38, 802 (1963).

[13]A. B. Bortz, M. H. Kalos, and J. L. Lebowitz, J. Comp. Phys. 17, 10 (1975).

[14]J. A. Baker, Phys. Rev. 129, 99 (1963).

[15]K. Binder, Physica (Utr.) 62, 508 (1972).
[16]M. Fisher (private communication).
[17]H. J. Leamy, G. H. Gilmer, and K. A. Jackson, Phys. Rev. Lett. 30, 601 (1973).
[18]K. Binder (private communication).
[19]J. S. Langer (private communication).
[20]D. de Fontaine, Ph.D. thesis (Northwestern University, 1967) (unpublished).
[21]A. J. Ardell, in *The Mechanics of Phase Transitions in Crystalline Solids* (Institute of Metals, London, 1969), Vol. 33, p. 111.
[22]John S. Huang, report at statistical mechanics meeting at Yeshiva University, 1975 (unpublished).
[23]John S. Huang, Walter I. Goldburg, and Allan W. Bjerkaas, Phys. Rev. Lett. 32, 921 (1974).