

RELEVANCE OF THE CAHN–HILLIARD–COOK THEORY AT EARLY TIMES IN SPINODAL DECOMPOSITION

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We analyse Cook's equation for spinodal decomposition and compare its predictions with computer-simulation data to conclude its formal consistency with the observations at early times. We thus provide a simple reference for the analysis of experiments at early, observable times and for the development of theory at late times.

A number of binary mixtures (including alloys such as Al–Zn, glassy and liquid mixtures, protein solutions, etc.) are known to undergo a process of phase segregation or *spinodal decomposition* when quenched to a thermodynamically unstable state [1–4]. The simulation in a computer of the time evolution of an Ising model with nearest-neighbor interactions ^{†1} produces a behavior qualitatively similar to the one in real materials [2–4]. Some characteristics of spinodal decomposition can thus be investigated by monitoring the structure function $S(\mathbf{k}, t)$ (where \mathbf{k} is a reciprocal wave vector and t the time after quenching) either experimentally by means of scattering from real materials or by numerical computations in the case of a model.

A simple linearized diffusion theory by Cahn and Hilliard [1] predicts the increase of $S(\mathbf{k}, t)$ in spinodal decomposition at an exponential rate for a fixed value of $|\mathbf{k}|$. Generally, however, one observes no significant time regime during the evolution of any (real or model) system which can be characterized by such an exponential growth. This fact has been explained by Langer and other [6] as a consequence of the importance of non-linear effects during phase segregation. There is then some hope [2] that exponential growth might be a characteristic of the very early evolution,

namely during a stage shorter than the time interval between quenching and the first observation in a typical experiment.

We compare here the predictions of the Cahn–Hilliard equation for the evolution of $S(\mathbf{k}, t)$, as reformulated by Cook to include thermodynamic fluctuations [7], with the data corresponding to the evolution of a finite Ising model with Kawasaki dynamics [3–5]. There is clear evidence that the Cahn–Hilliard–Cook (CHC) equation is formally consistent with the early evolution in spinodal decomposition, a fact which has been overlooked in the recent literature. We then argue that exponential growth of $S(\mathbf{k}, t)$ should only be observed, as an exception, in systems characterized by a large value for a given parameter k_c ; this could explain the reported, “untypical” behavior in a Lennard-Jones model [8]. The above fact provides a simple framework for the analysis of experimental results at early times where our knowledge is nowadays very scarce. At large enough values of t the experiments have shown that $S(\mathbf{k}, t)$ scales with time through some characteristic wave vector in the system [3]. The CHC equation becomes invalid in this late stage but the analysis in this letter may provide a hint for a modification of the CHC equation so that it incorporates the observed dynamical scaling [9].

The basic ingredients in the CHC theory [1,6,7] are a continuity equation $\partial\psi(\mathbf{r}, t)/\partial t = -\nabla \cdot \mathbf{J}(\mathbf{r}, t)$,

^{†1} For an earlier review see ref. [5].

where $\psi(r, t) = \eta(r, t) - \bar{\eta}$ measures local deviations of the composition η (fraction of the component A less the fraction of the component B in an A–B mixture) from the uniform state of mean composition $\bar{\eta}$, and a current density

$$J(r, t) = -M\nabla\{j[\psi(r, t), \nabla\psi(r, t)]\} + \xi(r, t). \quad (1)$$

Here $M > 0$ is the mobility, ξ is a (gaussian) stochastic force representing the direct influence of the thermal (phonon) reservoir on the atoms, and $j[\psi, \nabla\psi]$ is the drift which causes the interdiffusion of atomic species. Moreover it is assumed that, while the system is undergoing an irreversible process, it may be described by a Ginzburg–Landau free energy

$$F\{\psi\} = \int dr [\frac{1}{2}B(\nabla\psi)^2 + f(\psi)], \quad B > 0, \quad (2)$$

which incorporates inhomogeneity corrections (the first term within the integral) in addition to the local free-energy density $f(\psi)$ corresponding to the uniform state. Thus it follows [6,7] after linearization around $\bar{\eta}$ that

$$\partial S(k, t)/\partial t = -2Mk^2 [(A + Bk^2)S(k, t) - 1], \quad (3)$$

where $A \equiv (\partial^2 f/\partial \psi^2)_{\eta=\bar{\eta}}$.

The pioneering Cahn–Hilliard approach [1] disregards the fluctuations represented by ξ in eq. (1) thus leading to an equation which differs from eq. (3) in that the last term in the brackets is omitted. It then predicts that $S(k, t)$ will develop a maximum at $k = (-A/2B)^{1/2}$ which will grow exponentially with time. The *CHC equation* (3), on the contrary, has the solution

$$S(k, t) = \Omega^{-1}(k) + [S_0 - \Omega^{-1}(k)] \times \exp[-2Mk^2\Omega(k)t], \quad (4)$$

with $S_0 \equiv S(k, 0)$, which we shall assume is independent of k (as in the computer simulations where $S(k, 0) = 1 - \bar{\eta}^2$), and $\Omega(k) \equiv A + Bk^2$. The latter changes from positive to negative values at $k = k_c \equiv (-A/B)^{1/2}$ when $A < 0$. At $k > k_c$ one has $\Omega(k) > 0$ and $S(k, t)$ given by eq. (4) tends to an Ornstein–Zernike common envelope $\Omega^{-1}(k)$ when $t \rightarrow \infty$ ($M > 0$). In contrast with this relatively “slow” behavior, one has $\Omega(k) < 0$ at $k < k_c$ so that eq. (4) implies then an unbounded, generally non-observed exponential growth. Thus one may argue that (perhaps with some

exceptions; see e.g. ref. [8]) k_c is small enough in practice so that the most rapid growth of $S(k, t)$ is restricted to the smallest, unobservable values of k . In fact k_c depends on the phase point $(T, \bar{\eta})$ to which the system is quenched and we shall confirm later on that it is very close to zero for points in the neighborhood of the coexistence curve for the mixture.

Moreover, unlike the simpler equation by Cahn and Hilliard [1], eq. (4) predicts [9] that the maximum $k_m(t)$ of $S(k, t)$ decreases with time towards smaller values of k as in the case of real and model systems [4]; in fact $k_m(t)$ goes to $k_c/2^{1/2}$ when $t \rightarrow \infty$. One

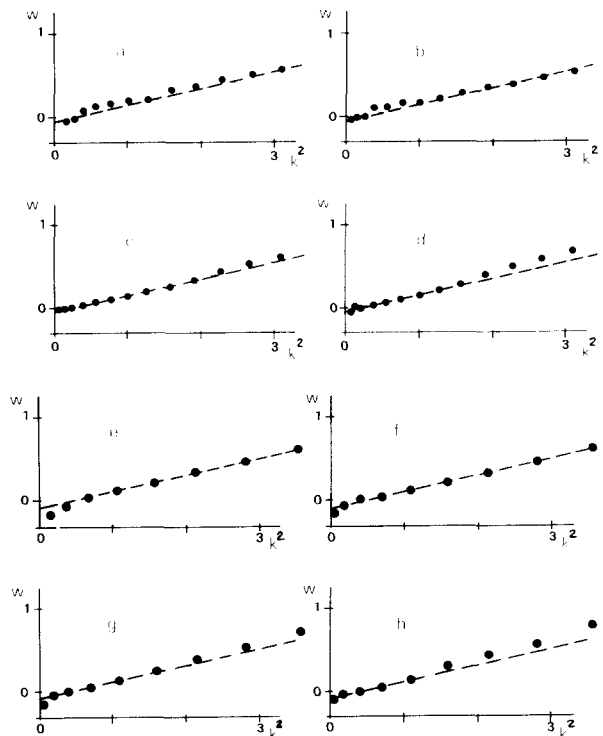


Fig. 1. The quantity $w = \Omega^c S_0$ defined in eq. (5) is plotted versus k^2 in some typical cases for M giving linear behavior at early times. A linear regression gives then the values reported for A and B in table 1. Note that Ω^c starts to deviate from $A + Bk^2$ when $t \approx t_c$. a, b, c and d correspond to $T = 0.59T_c$, $\rho = 0.10$, $M = 0.06S_0$ at times (in Monte Carlo units) $t = 30.4, 113.5, 454.5$ and 716.2 respectively; $t_c = 870$ in this case. e, f, g and h are for $T = 0.78T_c$, $\rho = 0.50$, $M = 0.09S_0$ at $t = 19.5, 77.1, 143.8$ and 213.6 respectively; $t_c = 200$. The situation is similar in the case of other phase points, but the linear regression $\Omega^c = A + Bk^2$ seems worse when closer to the coexistence curve, e.g. at $\rho = 0.05$, $T = 0.59T_c$ [9].

Table 1

Values for the parameters A , B and M obtained by fitting the CHC equation (4) to the data corresponding to the early ($t < t_c$) evolution of the model system in ref. [3] quenched to different phase points. The resulting fit is shown in fig. 2.

T/T_c	ρ	S_0	M/S_0	AS_0	BS_0	k_c	t_c
0.59	0.05	0.2256	0.06	-0.025	0.2	0.35	5200
0.59	0.075	0.2775	0.06	-0.05	0.2	0.50	1270
0.59	0.10	0.36	0.06	-0.06	0.2	0.55	870
0.59	0.20	0.64	0.08	-0.09	0.2	0.67	280
0.59	0.50	1	0.09	-0.18	0.2	0.95	56
0.78	0.50	1	0.09	-0.10	0.2	0.71	200
0.89	0.50	1	0.09	-0.04	0.2	0.45	1330

can convince oneself from eq. (4) that $t_c \equiv B(1 + AS_0)/MA^2$ is the time at which $k_m(t)$ crosses $k = k_c$. Thus one has $k_m(t) > k_c$ for $t < t_c$ and $S(k, t)$ shows then a "good", slow growth. The question is whether or not t_c corresponds to an observable value of the

time and we shall see that it does. The CHC equation (4) also implies the existence of a fixed point at $k = k_F \equiv [(1 - AS_0)/BS_0]^{1/2} > k_c$ in the $S(k, t)$ versus k curves, a fact which roughly [9] resembles the typical "cross-overs" observed experimentally in the tail of the structure function [5].

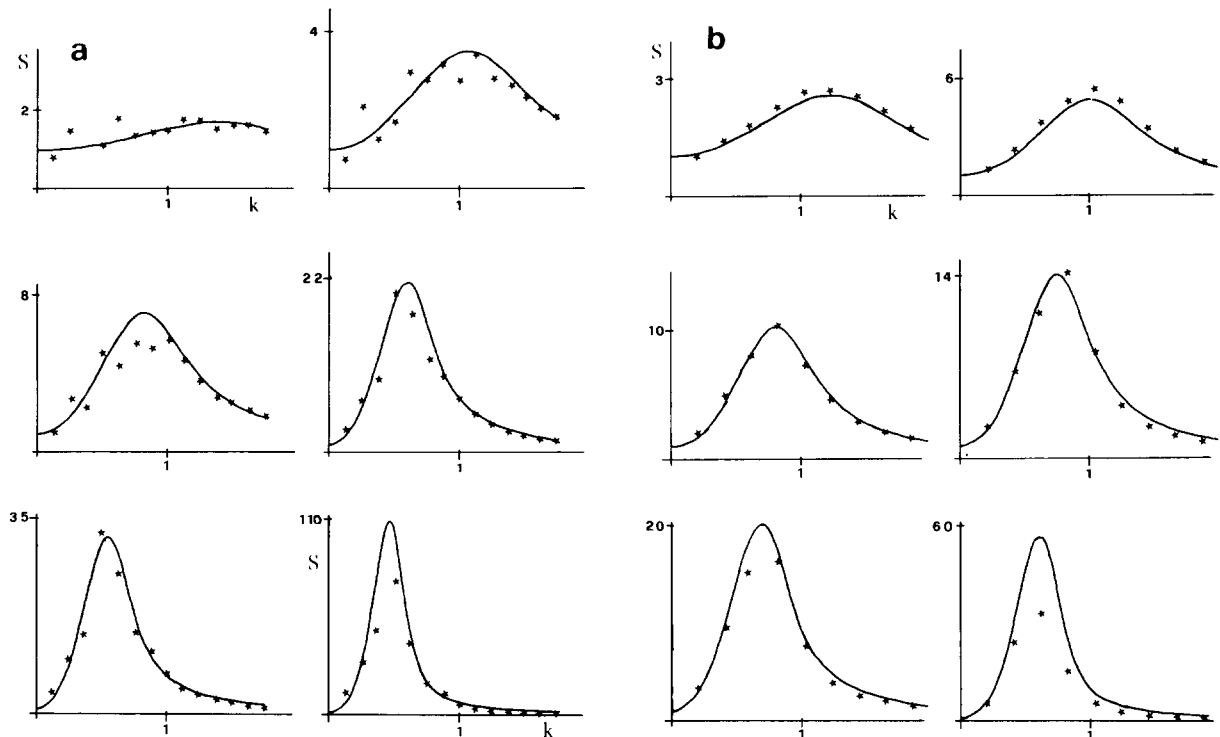


Fig. 2 (a) The structure function $S(k, t)$ versus k as given by the CHC equation (4) with the parameters in table 1 (solid line) is compared at different times ($t = 5.5, 30.4, 113.5, 556.9, 851.5$ and 2351.4 from the top to the bottom and from the right to the left respectively) with the data from the computer simulations in ref. [3] when $T = 0.59T_c, \rho = 0.10$. In this case $t_c = 870$ so that the last graph corresponds to a situation at $t \geq t_c$ when the CHC equation does not fit the data any more. (b) Same as (2) when $T = 0.78T_c, \rho = 0.50$ and $t = 9.2, 31.2, 94.6, 143.8, 213.6$ and 509.9 respectively; $t_c = 200$ in this case. Note that the fit of the CHC equation to the data in this case is even better for $t < t_c$ than the one reported in ref. [6].

In order to conclude quantitatively about the above facts we may define

$$\Omega^c = S^{-1}(k, t)[1 - (1/2Mk^2)\partial S(k, t)/\partial t] \quad (5)$$

and check whether or not there is a unique value for M such that: (i) Ω^c is independent of time, and (ii) Ω^c becomes linear in k^2 . If both conditions hold when Ω^c is computed from experimental data, it follows that the CHC equation (4) can describe the given data using the parameters from the linear regression $\Omega^c = A + Bk^2$.

We have checked this possibility by computing Ω^c from the data obtained in the computer simulations reported in refs. [3–5] which refer to a model (segregating) binary alloy with nearest-neighbor interactions. Conditions (i) and (ii) are seen to hold at “early” times only when M is around $0.1S_0$; one can then evaluate A and B , and the time limit t_c for the validity of the CHC description. Fig. 1 shows plots of $w = \Omega^c S_0$ versus k^2 in some typical cases. We find that $\Omega^c = A + Bk^2$, independent of time, holds when $t < t_c$ at any phase point, although the CHC equation seems a better description for points well inside the coexistence curve (“deep quenches” [3]) than for points close to it (“shallow quenches”). Table 1 gives our best values for A , B and M as a function of the temperature of quenching T and $\rho = (1 + \bar{\eta})/2$ (the density of A-atoms in the system).

The time t_c computed from the values for A , B and M in table 1 is not far from the time t_0 evaluated in ref. [3] for the onset of dynamical scaling in $S(k, t)$; as a consequence, the validity of the CHC equation should also be observable in real materials. As a matter of fact, the unit of time in the computer simulations seems [3,10] to correspond to more than 100 s in the case of Al–Zn alloys at low temperatures so that t_c

may correspond to several (or many) hours. Interestingly enough, our values for t_c seem to correspond to the same “amount of segregation” in the system [$p(t_c) \approx 0.54$] measured by the procedure proposed in fig. 4 of ref. [3].

Fig. 2 compares the behavior of the CHC equation with that of the computer-simulation data for some representative cases. One can also realize there how the CHC equation implies a faster growth of $S(k, t)$ when $t > t_c$ than the one in the model, as expected. We have checked, however, that the data can still be fitted with eq. (4) using a time-dependent parameter A after t_c ; the resulting analytic equation contains explicitly the property of dynamical scaling for $S(k, t)$; this will be reported elsewhere [9].

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