Eur. Phys. J. B **29**, 305–309 (2002)
DOI: 10.1140/epjb/e2002-00306-7

THE EUROPEAN
PHYSICAL JOURNAL B

Non-linear dynamics of spinodal decomposition

S. Villain-Guillot[1] and C. Josserand[2,a]

[1] Centre de Physique Moléculaire Optique et Hertzienne, Université Bordeaux I, 33406 Talence Cedex, France
[2] Laboratoire de Modélisation en Mécanique[b], Université Pierre et Marie Curie, 8 rue du Capitaine Scott, 75015 Paris, France

Received 16 October 2001 / Received in final form 15 March 2002

Abstract. We develop a new technique describing the non linear growth of interfaces. We apply this analytical approach to the one dimensional Cahn-Hilliard equation. The dynamics is captured through a solvability condition performed over a particular family of quasi-static solutions. The main result is that the dynamics along this particular class of solutions can be expressed in terms of a simple ordinary differential equation. The density profile of the stationary regime found at the end of the non-linear growth is also well characterized. Numerical simulations are compared in a satisfactory way with the analytical results through three different fitting methods and asymptotic dynamics are well recovered, even far from the region where the approximations hold.

PACS. 05.45.Yv Solitons – 47.20.Ky Nonlinearity – 47.54.+r Pattern selection; pattern formation

Phase transitions arise when a homogeneous system is turned into a thermodynamically unstable regime. The homogeneous phase separates for example into two different phases, giving rise to interfaces dynamics or pattern formation. The dynamics of this separation can be classified into nucleation process (cavitation) and spinodal decomposition, occurring in problems as varied as binary alloys, vapor condensation [1], ferromagnetic Ising model [2] or thin films of copolymers [3]. Quite some time ago Hillert [4], Cahn and Hilliard [5] proposed a model which became very well know describing the dynamics of the segregation for binary mixtures [6]. It corresponds to Model B in the Hohenberg and Halperin's classification [2], for a conserved order parameter. The resulting partial differential equation has been used to explain the dynamics of pattern formation, and has been applied to phase transition in liquid crystals [7], or segregation of granular mixtures in a rotating drum [8].

The kinetics, associated with the phase transition is usually composed of three stages: first, the linear instability of the system leads to a creation of a modulation of the order parameter at a well defined length scale. A different (non linear) dynamical stage follows: the growth of the modulation saturates and a pattern composed of well defined interfaces is obtained. Finally, at the late stage, the different domains interact in a coalescence process; the number of domains diminishes ending up into two well-separated phases.

Numerical simulations of the Cahn-Hilliard (C-H) equation modeling the dynamics after a quench in temperature are shown in Figure 1, where the three stages described above are well distinguished: exponential growth of the fluctuations around a well defined wave length (observe the length scale selection from Fig. 1a to b), then non-linear growth and its saturation Figure 1c (during this stage, the typical length scale of the modulation does not change significantly and is often considered as constant). After saturation, the dynamics is dominated by the coalescence of domains as shown from Figure 1c to d.

Numerous works on phase transition have been devoted to the coarsening dynamics, predicting the kinetics of $L(t)$, the macroscopic size of the domains. For instance, for (C-H), scaling arguments and stability criterion give the law $L(t) \sim t^{1/3}$ for spatial dimension greater than one and a logarithm behavior for one dimension [9].

In this paper, we focus on the less studied second stage of spinodal decomposition, applied for the Cahn-Hilliard equation in one spatial dimension. We work with a constant diffusion coefficient, contrary to previous studies [10]. Using an ansatz based on the so-called soliton lattice, we develop, *via* a solvability criterion, an analytical approach valid for the region closed to the critical point (*i.e.*, for a symmetric mixture). A simple ordinary differential equation is obtained, describing the full dynamics. Its integration is in very good agreement with numerical simulations and in qualitative agreement with the scenario suggested by AFM experiments for spinodal decomposition in mixtures of block co-polymers [3]. In addition, it

---

[a] e-mail: `josseran@lmm.jussieu.fr`

[b] UMR CNRS 7607

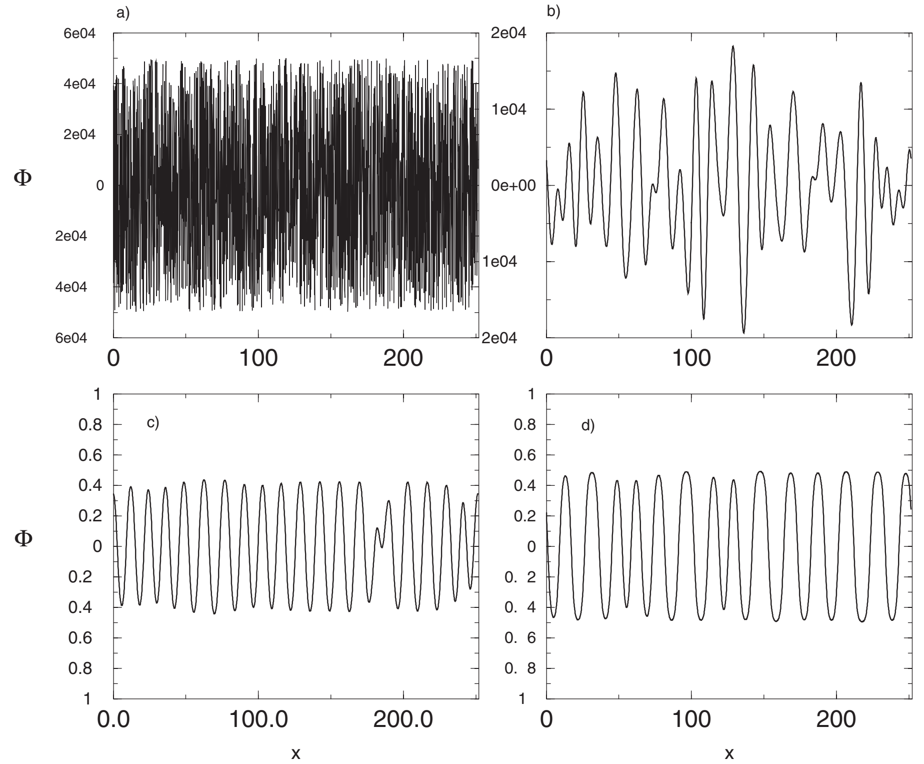

Fig. 1. Time evolution of the order parameter $\Phi(x,t)$ for $\varepsilon = -1$, $dx = 0.1227$. (a) initial conditions at $t = 0$ are taken randomly with a very low amplitude (5×10^{-4}); (b) at time $t = 15$, the amplitude of the modulation has decreased, while only long wavelength contributions are still present. The small scales perturbations have been damped by the (C-H) dynamics; (c) at $t = 225$, the modulation has almost reached its final amplitude, keeping roughly the same number of peaks as before; (d) at $t = 1800$, the coarsening process has reduced slightly the number of domains.

predicts the density profile associated with the stationary regime which ends this non-linear growth.

The Cahn-Hilliard theory results in a modified diffusion equation:

$$\frac{\partial \Phi}{\partial t}(x,t) = \nabla^2 \left(\frac{\delta F}{\delta \Phi}\right) = \nabla^2 \left(\frac{\varepsilon}{2}\Phi + 2\Phi^3 - \nabla^2 \Phi\right). \quad (1)$$

Here Φ is the real order parameter and ε the dimensionless control parameter (for example, a reduced temperature). This equation has been derived from microscopic consideration by Langer [11].

Spinodal decomposition is the dynamics by which phase separation occurs when a system is quenched into a thermodynamically unstable state. Equation (1) models this mechanism if one changes suddenly (at time $t = 0$), from a positive value of ε to a negative one. Starting at time $t = 0$ with a random initial condition of small amplitude, the system will separate into the two thermodynamically stable phases with corresponding amplitudes $\Phi = \pm\frac{\sqrt{-\varepsilon}}{2}$. If the density distribution is considered as a sum of Fourier modes:

$$\Phi(x,t) = \sum_q \phi_q \mathrm{e}^{\mathrm{i}qx+\sigma t}$$

then, linearizing equation (1) around the homogeneous solution $\Phi = 0$ (*i.e.* neglecting the non linear term Φ^3), we obtain the amplification factor $\sigma(q) = -(q^2 + \frac{\varepsilon}{2})q^2$. For $\varepsilon > 0$, $\sigma(q)$ is negative for all q, and $\Phi = 0$ is the only solution. For $\varepsilon < 0$, σ is positive for $q < \sqrt{\frac{-\varepsilon}{2}}$ and the perturbation of larger wavelength can grow exponentially in time. On the other hands, the small wavelength perturbations are damped as it can be seen between Figure 1a and b. The fastest amplification factor is reached for $q = q_{\max} = \frac{\sqrt{-\varepsilon}}{2}$ (with $\sigma_{\max} = \frac{\varepsilon^2}{16}$). This maximum amplification factor dominates the first stage of the dynamics and explains why the modulations appear at a well defined wave length.

For $\varepsilon < 0$, equation (1) admits in fact a family of stationary solution, the so-called soliton-lattice [12]:

$$\Phi_{k,\varepsilon}(x) = k\Delta \mathrm{Sn}\left(\frac{x}{\xi}, k\right) \text{ with } \xi = \frac{1}{\Delta} = \sqrt{2\frac{k^2+1}{-\varepsilon}} \quad (2)$$

where $\mathrm{Sn}(x,k)$ is the Jacobian elliptic function sine-amplitude. This family of solutions is parametrized by ε and the modulus $k \in [0,1]$. These solutions describe a periodic pattern of period

$$T = 4K(k)\xi, \text{ where } K(k) = \int_0^{\frac{\pi}{2}} \frac{\mathrm{d}t}{\sqrt{1 - k^2 \sin^2 t}} \quad (3)$$

is the complete Jacobian elliptic integral of the first kind. The soliton-lattice solution can be associated with a phase segregation locally limited by the finite diffusion coefficient. For $k=1$, we recover the usual interface:

$$\Phi(x) = \frac{\sqrt{|\varepsilon|}}{2} \tanh\left(\frac{\sqrt{|\varepsilon|}}{2} x\right).$$

In the limit $k \to 0$, it describes a small-amplitude sinusoidal modulation:

$$\Phi_{k,\varepsilon}(x) = k\sqrt{\frac{|\varepsilon|}{2}} \sin\left(\sqrt{\frac{|\varepsilon|}{2}} x\right).$$

The particular study of the non linear growth can be simplified by taking advantage of the observation that the kinetics occurs almost at constant wave length. In fact, in one and two dimensions, one observes a pattern of bubbles of quite homogeneous size, which is somehow frozen during the growth (only the amplitude of the pattern evolves). The time for this evolution scales like $1/\sigma_{max}$, while the coalescence dynamics is a self-inhibiting process; it is then reasonable to consider that the periodicity of the structures remain constant during the finite time of the growth. Thus we now seek to solve in one dimension equation (1) for a fixed temperature ε_0:

$$\frac{\partial \Phi}{\partial t}(x,t) = 2\partial_{xx}\left(\frac{\varepsilon_0}{2}\Phi + 2\Phi^3 - \partial_{xx}\Phi\right), \tag{4}$$

while restricting the periodicity of the modulation to be strictly constant and defined by $T = 4\pi\sqrt{\frac{-1}{\varepsilon_0}}$ associated with $q_{max} = \frac{\sqrt{|\varepsilon_0|}}{2}$. Initial conditions should be the sine mode $\sin(q_{max}x)$ with a small amplitude μ ($\mu \ll \sqrt{\varepsilon_0/2}$). We now make the *ansatz* that these solutions, at first order, belong at any time to the two parameters family of solutions Φ_{k,ε^*}, with k and ε^* being functions of time. Since the period is chosen to be constant, using equations (2, 3), we find that k and ε^* are related one to each other through:

$$\varepsilon^* = \varepsilon^*(k) = 2(1+k^2)\varepsilon_0 K^2(k)/\pi^2. \tag{5}$$

Eventually, we have selected a one parameter subfamily of solutions of given spatial periodicity (that we will call $\Psi^*(x,k)$ later on):

$$\Psi^*(x,k) = \frac{\sqrt{-\varepsilon_0}}{\pi} k K(k) \mathrm{Sn}\left(\frac{\sqrt{-\varepsilon_0}K(k)}{\pi}x, k\right).$$

The dynamics of $\Phi(x,t)$ has been reduced to the evolution of $k(t)$ (or $\varepsilon^*(t)$). Given a function Φ (obtained either from experimental data or numerical simulation of equation (4)) at time t, the *ansatz* assumes that there exists a k so that $\Phi(x,t) \sim \Psi^*(x,k)$. For this purpose, we developed three different algorithms, making use of general properties of the family of solutions $\Phi_{k,\varepsilon}$: k can be deduced both from the amplitude of the oscillation equals to $\frac{\sqrt{-\varepsilon_0}}{\pi}kK(k)$ or from the relation $k = 1 - \left((\Phi(T/2,t)/\Phi(T/4,t))^2 - 1\right)^2$; on the other hand a straightforward computation relates k to the ratio of the two first terms of the Fourier transform of Φ. These three methods give similar results within an error of one percent. However, the validity of the ansatz has still to be checked by comparing the initial function $\Phi(x,t)$ with the extrapolated function $\Psi^*(x,k)$ obtained by one of these three procedures. It is shown in Figure 2 for two different times of a numerical simulation of (4); we observed that the relative differences between the two function is less than 0.01.

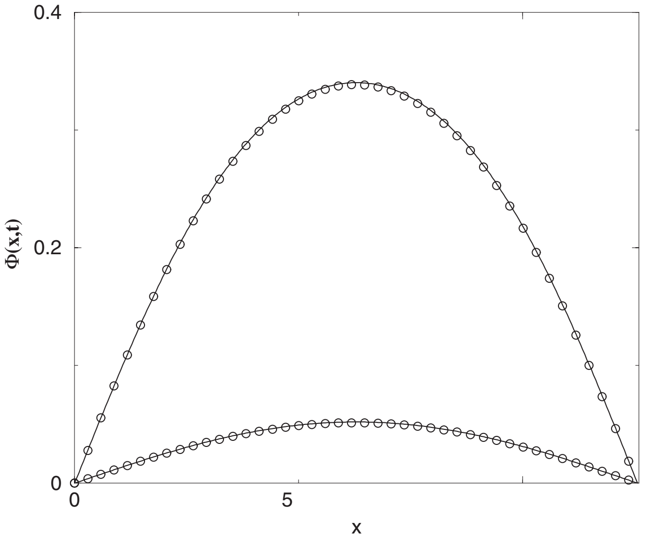

Fig. 2. Comparison for time $t = 100$ and $t = 140$ between the numerical solution of (4) (circles) and the functions $\Psi^*(x,k)$, with k extrapolated from the Fourier transform of $\Phi(x,t)$. Initial conditions are taken to be $\mu = 10^{-4}$.

The aim of this work is to show that $k(t)$ can be deduced analytically, *via* an explicit ordinary differential equation. Therefore, in what follows, we will seek the solution of (4) in the form:

$$\Phi(x,t) = \Psi^*(x,k(t)) + \eta\varphi(x,t) \tag{6}$$

where φ accounts for high order correction terms to Ψ^*, while the "ansatz" assumes that $\eta \ll 1$.

$\varepsilon^*(t)$ can be interpreted as a fictitious temperature: it is the temperature extracted from the profile at a given time, using equation (5). Initial conditions correspond to the limit $k \to 0$ and the equivalent temperature $\frac{\varepsilon_0}{2}$. In order to describe the evolution of the modulus $k(t)$, or equivalently the dynamics for $\varepsilon^*(t)$, we will use the so-called solvability condition technique. Substituting formula (6) in the Cahn-Hilliard equation (4) gives the following dynamics:

$$\frac{\partial \Phi}{\partial t}(x,t) = \frac{\partial \Psi^*}{\partial k}\frac{\mathrm{d}k}{\mathrm{d}t} + \eta\frac{\partial}{\partial t}\varphi =$$
$$\frac{\partial^2}{\partial x^2}\left(\frac{\varepsilon_0}{2}\Psi^* + 2\Psi^{*3} - \nabla^2\Psi^* + \eta\left(\frac{\varepsilon_0}{2}\varphi + 6\Psi^{*2}\varphi - \nabla^2\varphi\right)\right).$$

where we have kept only the lowest order terms in the perturbation. As $\Psi^*(x,k(t))$ satisfies the relation:

$$\varepsilon^*(k)\Psi^* + 4\Psi^{*3} - 2\nabla^2\Psi^* = 0,$$

we then have the following dynamics:

$$\frac{\partial\Psi^*}{\partial k}\frac{\mathrm{d}k}{\mathrm{d}t}+(\varepsilon^*-\varepsilon_0)\frac{\partial^2\Psi^*}{\partial x^2}+\eta\frac{\partial}{\partial t}\varphi = \eta\frac{\partial^2}{\partial x^2}(\frac{\varepsilon_0}{2}\varphi+6\Psi^{*2}\varphi-\nabla^2\varphi).$$

The balance of the different terms gives the small parameter of the expansion $\eta\sim\varepsilon^*-\varepsilon_0$; we obtain $\frac{\mathrm{d}k}{\mathrm{d}t}\sim\eta$ and $\partial_t\varphi\sim\eta\varphi$. Neglecting the terms of order η^2 in the previous equation, we end up solving the linear system:

$$\frac{\partial^2}{\partial x^2}(\mathcal{L}\varphi)=\frac{\partial\Psi^*}{\partial k}\frac{\mathrm{d}k}{\mathrm{d}t}+(\varepsilon^*-\varepsilon_0)\frac{\partial^2}{\partial x^2}\Psi^*$$

where, $\mathcal{L}$ is the linearized C-H operator $\mathcal{L}\varphi = \left(\frac{\varepsilon^*}{2}+6\Psi^{*2}-\nabla^2\right)\varphi$. Strictly speaking, this analysis is valid only for $\varepsilon\sim\varepsilon_0$; however, it is a classical assumption of solvability condition (confirmed below by the numerical results presented in Fig. 3) to expand it for the whole dynamics. A necessary condition for solution is that the right hand side of the system is orthogonal to the kernel of the adjoint operator $(\partial_{x^2}\mathcal{L})^\dagger$. Indeed, defining the scalar product over one period T as:

$$\langle f|g\rangle=\int_0^T f(x)g(x)\mathrm{d}x$$

we obtain for any distribution $f\in\mathrm{Ker}((\frac{\partial^2}{\partial x^2}\mathcal{L})^+)$:

$$\begin{aligned}\left\langle f\mid\frac{\partial\Psi^*}{\partial k}\cdot\frac{\mathrm{d}k}{\mathrm{d}t}+(\varepsilon^*-\varepsilon_0)\frac{\partial^2}{\partial x^2}\Psi^*\right\rangle &= \left\langle f\mid\frac{\partial^2}{\partial x^2}\mathcal{L}\left(\varphi\right)\right\rangle\\ &= \left\langle\left(\frac{\partial^2}{\partial x^2}\mathcal{L}\right)^+ f\mid\varphi\right\rangle=0.\end{aligned}$$

Since $\mathcal{L}$ is a self-adjoint operator, we have $(\frac{\partial^2}{\partial x^2}\mathcal{L})^+ = \mathcal{L}\frac{\partial^2}{\partial x^2}$. Therefore we are looking for function f, such that $\frac{\partial^2}{\partial x^2}f\in\mathrm{Ker}(\mathcal{L})$. The Goldstone mode $\partial_k\Phi_{k,\varepsilon^*}$, for $\varepsilon=\varepsilon^*=$const., is an element of $\mathrm{Ker}(\mathcal{L}^\dagger)$, and if we consider the distribution $\chi(x,t)$, such that $\frac{\partial^2}{\partial x^2}\chi(x,t)=\Phi_{k,\varepsilon^*}(x)$, then $\partial_k\chi\in\mathrm{Ker}((\partial_{x^2}\mathcal{L})^\dagger)$. Thus, we obtain the desired equation for $\frac{\mathrm{d}k}{\mathrm{d}t}$:

$$\begin{aligned}\langle\partial_k\chi\mid\partial_k\Psi^*\rangle\frac{\mathrm{d}k}{\mathrm{d}t} &= (\varepsilon_0-\varepsilon^*)\langle\partial_k\chi\mid\partial_{x^2}\Phi_{k,\varepsilon^*}\rangle\\ &= \frac{\varepsilon_0-\varepsilon^*}{\pi}|\varepsilon_0|^{-\frac{1}{2}}\frac{kK(k)}{1+k^2}\\ &\quad\times\left(\frac{2E(k)}{1-k^2}-K(k)\right),\end{aligned}\qquad(7)$$

where $E(k)=\int_0^{\frac{\pi}{2}}\sqrt{1-k^2\sin^2 x}\,\mathrm{d}x$ is the complete Jacobian elliptic integral of the second kind. The l.h.s can be expressed using $\psi(x,t)$, defined as $\frac{\partial}{\partial x}\psi=\Psi^*$, and which reads:

$$\psi\left(x,t\right)=\ln\left(\mathrm{Dn}\left(\frac{x}{\xi},k\right)-k\mathrm{Cn}\left(\frac{x}{\xi},k\right)\right)-\frac{1}{2}\ln(1-k^2).$$

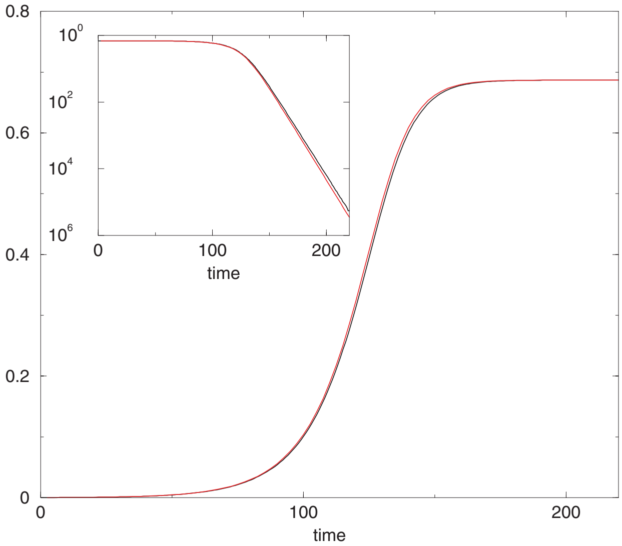

Fig. 3. Comparison between the solution of the ordinary differential equation (8) for the modulus $k(t)$ (gray curve) and the modulus extracted from the full (C-H) dynamics (black line) with the same initial condition $k(0)=2\times10^{-4}$. The dynamics converges to k_s in both case for large time. The inset shows the exponential convergence of both curves in asymptotic regime, where the solubility condition is valid; it compares well with $k_s-k(t)\sim\mathrm{e}^{-\varepsilon_0^2 t/8}$; in addition, far from k_s, the exponential growth for small time $k(t)\sim\mathrm{e}^{-\varepsilon_0^2 t/16}$ is also retrieved by equation (8).

Cn and Dn are the Jacobi elliptic function cosine and delta amplitudes respectively. Finally:

$$\langle\partial_k\chi\mid\partial_k\Psi_{k,\varepsilon^*}\rangle=-\langle\partial_k\psi\mid\partial_k\psi\rangle=-|\varepsilon_0|^{-\frac{1}{2}}I(k)$$

where $I(k)$ is independent of ε_0. Equation (7) can be eventually recast in the following differential equation for $k(t)$:

$$\begin{aligned}\frac{\mathrm{d}k}{\mathrm{d}t} &= \frac{{\varepsilon_0}^2 kK(k)}{\pi I(k)}\\ &\quad\times\left(\frac{2}{(1+k^2)}-\left(\frac{2K(k)}{\pi}\right)^2\right)(\frac{2E(k)}{1-k^2}-K(k)).\end{aligned}\qquad(8)$$

This equation provides the time scale dependence in ε_0^{-2} for the dynamics, already predicted by the (C-H) linear theory. The r.h.s. is in fact proportional to $\varepsilon_0-\varepsilon^*$, and the dynamics ends when the fictitious temperature reaches the thermodynamical one ε_0; this occurs when k^2 is equal to $k_s^2=0.471941$ which is solution of the equation $K(k)\sqrt{2\left(1+k^2\right)}=\pi$. Thus, the asymptotic steady state solution of equation (4) for a given period is: $\lim_{t\to\infty}\Phi(x,t)=\Psi^*(x,k_s)$. It corresponds to the end of the non-linear growth (in Fig. 1c) and the value of k_s associated with this steady state is retrieved numerically by the three methods explained above. Equation (8) can be solved numerically. The result, displayed on Figure 3 shows good agreement with the numerical simulations of

(C-H). Particularly, the exponential convergence to k_s is well described (see the inset of Fig. 3). Moreover, equation (8) remains valid even for k far from k_s, since the exponential growth for small k is exactly found (corresponding to $\sigma_{max} = \varepsilon_0^2/16$).

We have shown that the choice of an ansatz within the soliton-lattice family allows a reliable description of the one dimensional dynamics of the spinodal decomposition, valid even for the early stage of the dynamics. Contrary to reference [14], our ansatz rely on the hypothesis that during the first two stages of the dynamics, the periodicity of the order parameter remains constant. In this sense, it is an adiabatic ansatz. The validity of the assumptions has been investigated in details (see also Ref. [13]) and checked numerically (see Fig. 2). It enables to model the non-linear growth starting with spatial random initial conditions and predicts the stationary profile $\Psi^*_{k_s}$. Only after the order parameter distribution has reached this specific profile, starts the noise to be pertinent for the dynamics; it can be modeled by a random noise term added at the r.h.s. of equation (1), as was shown by Langer. Although this profile might not be observable in a usual phase transition due to its instability [11], it might be relevant for the axial segregation in rotating drums [15], where the dynamics ends after the second stage.

The use of the solvability technique combined with the choice of an adiabatic ansatz might be generalized to the study of other non linear dynamics. For instance, spinodal decomposition in superfluid Helium or Bose condensate has been argued to be described by a cubic-quintic non linear equation [16]; in this particular case, one needs to retrieve a relevant soliton-like family of solutions along which to compute the adiabatic dynamics. The same difficulties would arise when the method is adapted to higher space dimensions. However, these questions are postponed for future studies.

Finally, this approach could be used to explore the self-similar scenario for coalescence depicted in reference [3], starting with the previous stationary distribution as initial condition. The only change will be in the use of a family of ansatz of growing periodicity T_n, which would also be a slow variable of the position, since the coalescence is controlled by local interactions of the pattern [17]: indeed, numerical studies [13] seem to show for late times the generation of higher harmonics which could be associated with this self-similar scenario.

The authors are grateful to David Andelman and Sergio Rica for helpful discussions.

References

1. J.S. Langer, in *Solids Far From Equilibrium*, edited by C. Godrèche (Cambridge, 1992)
2. P.C. Hohenberg, B.I. Halperin, Rev. Mod. Phys. **49**, 435 (1977). For a review, see J.D. Gunton, M. San Miguel, P.S. Sahni, in *Phase Transition and Critical Phenomena*, edited by C. Domb, J.L. Lebowitz (Academic, London, 1983), Vol. 8, p. 267
3. S. Joly, A. Raquois, F. Paris, B. Hamdoun, L. Auvray, D. Ausserre, Y. Gallot, Phys. Rev. Lett. **77**, 4394 (1996)
4. M. Hillert, Acta Met. **9**, 525 (1961)
5. J.W. Cahn, J.E. Hilliard, J. Chem. Phys. **28**, 258 (1958)
6. C. Wagner, Z. Electrochem. **65**, 581 (1961)
7. C. Chevallard, M. Clerc, P. Coullet, J.M. Gilli, Eur. Phys. J. E **1**, 179 (2000)
8. S. Puri, H. Hayakawa, `cond-mat/9901260`
9. I.M. Lifshitz, V.V. Slyozov, J. Phys. Chem. Solids **19**, 35 (1961). A.J. Bray, Adv. Phys. **43**, 357 (1994)
10. A. Novik-Cohen, L.A. Segel, Physica D **10**, 277 (1984). R. Mauri, R. Shinnar, G. Triantafyllou, Phys. Rev. E **53**, 2613 (1996)
11. J.S. Langer, Ann. Phys. **65**, 53 (1971)
12. A.I Buzdin, V.V. Tugushev, Sov. Phys. JETP **58**, 428 (1983). A. Saxena, A.R. Bishop, Phys. Rev. A **44**, R2251 (1991)
13. S. Villain-Guillot, C. Josserand, in preparation
14. J.S. Langer, M. Bar-on, H.D. Miller, Phys. Rev. A **11**, 1417 (1975)
15. Y. Oyama, Bull. Inst. Phys. Chem. Res. Rep. **5**, 600 (1939)
16. C. Josserand, S. Rica, Phys. Rev. Lett. **78**, 1215 (1997)
17. A.A. Fraerman, A.S. Mel'nikov, I.M. Nefedov, I.A. Shereshevskii, A.V. Shpiro, Phys. Rev. B **55**, 6316 (1997)