Macromol. Symp. ***160,*** *215–223 (2000)*

Non-linear Dynamics of Spinodal Decomposition

E. Prostomolotova, I. Erukhimovich *

Physics Department, Moscow State University, 119899, Moscow, Russia

SUMMARY: A new approach is proposed to describe the spinodal decomposition, in particular, in polymer binary blends. In the framework of this approach, the spinodal decomposition is described as a relaxation of one-time structure factor S(q,t) treated as an independent dynamic object (a peculiar two-point order parameter). The dynamic equation for S(q,t), including the explicit expression for the corresponding effective kinetic coefficient, is derived. In the first approximation this equation is identical to the Langer equation. We first solved it both in terms of higher transcendental functions and numerically. The asymptotic behaviour of S(q,t) at large (from the onset of spinodal decomposition) times is analytically described. The values obtained for the power-law growth exponent for the large-time peak value and position of S(q,t) are in good agreement with experimental data and results of numerical integration of the Cahn-Hilliard equation.

Basic concepts

The problem of spinodal decomposition, i.e. dynamics of the systems described by Landau Hamiltonian beyond the region of their spatially homogeneous (uniform) state stability, arises in many physical applications. The free energy of these systems may be written in terms of the continual integral

$$F = -kT \ln \frac{\int \delta\varphi \exp(-\Phi(\{\varphi(\mathbf{r})\},T)/(kT))}{\int \delta\varphi \exp(-\int d\mathbf{x}\varphi(\mathbf{x})\hat{\Gamma}_0\varphi(\mathbf{x})/2)}, \qquad (1)$$

where T is temperature, k is the Boltzmann constant (henceforth we set $k = 1$) and

$$\Phi(\{\varphi(\mathbf{r})\},T) = T\left(\frac{\int d\mathbf{x}\,\varphi(\mathbf{x})\,\hat{\Gamma}\,\varphi(\mathbf{x})}{2} + \int d\mathbf{x}\left(\frac{\alpha\varphi^3}{3!} + \frac{\beta\varphi^4}{4!}\right)\right) \qquad (2)$$

is the Landau Hamiltonian having meaning of the *virtual* free energy of the system in a state with a fixed non-uniform spatial distribution of the order parameter $\{\varphi(\mathbf{r})\}$ assumed for simplicity to be scalar. The Fourier-transforms of the kernels Γ and Γ_0 of the integral operators $\hat{\Gamma}_0\varphi(\mathbf{x}) = \int d\mathbf{x}'\,\Gamma_0(\mathbf{x}-\mathbf{x}')\,\varphi(\mathbf{x}')$ and $\hat{\Gamma}\varphi(\mathbf{x}) = \int d\mathbf{x}'\,\Gamma(\mathbf{x}-\mathbf{x}')\,\varphi(\mathbf{x}')$ appear as follows:

$$\Gamma(q) = \int d\mathbf{x}\,\Gamma(\mathbf{x})\exp(i\mathbf{qx}) = \tau + Q^2, \qquad \Gamma_0(q) = \tau_0 + Q^2, \qquad Q^2 = a^2q^2, \qquad (3)$$

CCC 1022-1360/00/$ 17.50+.50/0

Here $\alpha, \beta > 0$ and $a^2 > 0$ are phenomenological constants and dimensionless temperature $\tau = \left(T - T_{cr}\right)/T_{cr}$ characterises the state of the system with respect to its instability region corresponding to $\tau < 0$.

The traditional statement of the spinodal decomposition problem is as follows [1-3]. Until initial time $t = 0$ the system is fixed at certain initial temperature $\tau=\tau_0>0$ and distribution $\varphi_0(\mathbf{r})$. Then the temperature drops instantly till a value $\tau=\tau_1<0$, the subsequent evolution is supposed to obey the well-known phenomenological Cahn-Hilliard equation 1):

$$\partial\varphi(\mathbf{y},t)/\partial t = -\hat{\Lambda}\delta\Phi\left(T,\{\varphi(\mathbf{x},t)\}\right)/\delta\varphi(\mathbf{y},t) \qquad (4)$$

$\hat{\Lambda} = -\Lambda_0\nabla^2$ is the kinetic coefficient of the blend as an operator. The numerical solution of this equation for different realisations of the initial 2D distribution $\varphi_0(\mathbf{x})$ showed 4) that the average of the order parameter $\varphi(\mathbf{x},t)$ over k different $\varphi_0(\mathbf{x})$ approaches zero when $k \to \infty$ (which imitates averaging over the large volume of the demixing system). Therewith, the averaged structure factor $\mathrm{S}(q,t)$ in the Fourier space acquires a rather definite radially symmetric shape. This fact suggests that it could be more appropriate to look for and analyse the relaxation equation describing directly the structure factor evolution.

Dynamic Equations for Virtual and Thermodynamic Structure Factor

We introduce the *virtual* correlation function of a binary system and Fourier-transform of the former (called *virtual* structure factor) as follows:

$$G(\mathbf{x}) = \int\varphi(\mathbf{x}')\varphi(\mathbf{x}'+\mathbf{x})d\mathbf{x}'/V, \qquad (5)$$

$$\mathrm{S}(\mathbf{q}) = \int d\mathbf{x}\, G(\mathbf{x})\exp(i\mathbf{q}\mathbf{x}) = \phi(\mathbf{q})\,\phi(-\mathbf{q})/V, \qquad (6)$$

where $\varphi(\mathbf{y})$ is the local value of the volume fraction of component A in the point $\mathbf{y}$ and $\phi(\mathbf{q}) = \int d\mathbf{x}\,\varphi(\mathbf{x})\exp(i\mathbf{q}\mathbf{x})$. To obtain the dynamic equation governing the virtual structure factor relaxation, we take the derivative of the definition (5) with respect to time:

$$\frac{\partial G(\mathbf{x})}{\partial t} = \frac{1}{V}\int\left[\frac{\partial\varphi(\mathbf{y})}{\partial t}\varphi(\mathbf{x}+\mathbf{y}) + \varphi(\mathbf{y})\frac{\partial\varphi(\mathbf{y}+\mathbf{x})}{\partial t}\right]dy = \frac{1}{V}\int\frac{\partial\varphi(\mathbf{y})}{\partial t}\left[\varphi(\mathbf{x}+\mathbf{y}) + \varphi(\mathbf{y}-\mathbf{x})\right]dy \qquad (7)$$

and substitute into (7) the Cahn-Hilliard equation (4) which yields:

$$\frac{\partial G(\mathbf{x})}{\partial t} = \frac{\Lambda_0}{TV}\int(\varphi(\mathbf{y}+\mathbf{x})+\varphi(\mathbf{y}-\mathbf{x}))\left(\frac{\partial^2}{\partial \mathbf{y}^2}\frac{\delta\Phi}{\delta\varphi(\mathbf{y})}\right)d\mathbf{y} \tag{8}$$

(We assumed for simplicity the kinetic coefficient Λ_0 to be space-independent.)

Note now, that the free energy of non-uniform polymer system can be represented in the form of both the functional (2) of the order parameter distribution $\{\varphi(\mathbf{x})\}$ and a functional Ω of the virtual correlation function (5), the functionals Φ and Ω being interelated as follows:

$$\int\frac{\delta\Phi(\{\varphi(\mathbf{x})\})}{\delta\varphi(\mathbf{y})}\delta\varphi(\mathbf{y})d\mathbf{y} = \int\frac{\delta\Omega(\{G(\mathbf{x})\})}{\delta G(\mathbf{z})}\delta G(\mathbf{z})d\mathbf{z} = \int\frac{\delta\Omega(\{G(\mathbf{x})\})}{\delta G(\mathbf{z})}\frac{\delta G(\mathbf{z})}{\delta\varphi(\mathbf{y})}\delta\varphi(\mathbf{y})d\mathbf{z}\,d\mathbf{y} \tag{9}$$

On the other hand, it follows from definition (5) that

$$\delta G(\mathbf{z})/\delta\varphi(\mathbf{y}) = (\varphi(\mathbf{z}+\mathbf{y})+\varphi(\mathbf{y}-\mathbf{z}))/V\,.$$

Substituting it into (8) and (9) we obtain

$$\frac{\partial G(\mathbf{x})}{\partial t} = \frac{1}{V^2}\frac{\Lambda_0}{T}\int\int(\varphi(\mathbf{y}+\mathbf{x})+\varphi(\mathbf{y}-\mathbf{x}))\frac{\delta\Omega}{\delta G(\mathbf{z})}\frac{\partial^2}{\partial \mathbf{y}^2}(\varphi(\mathbf{y}+\mathbf{z})+\varphi(\mathbf{y}-\mathbf{z}))d\mathbf{y}d\mathbf{z} \tag{10}$$

which is finally reduced by Fourier-transform to the desired equation:

$$\partial \mathrm{S}(\mathbf{q})/\partial t = -T^{-1}\,\tilde{\Lambda}(q,\{\mathrm{S}(\mathbf{q})\})\,\delta F/\delta \mathrm{S}(\mathbf{q}) \tag{11}$$

where F is specific (per unit volume) free energy as a functional of the virtual structure factor $\mathrm{S}(q)$ and an effective kinetic coefficient $\tilde{\Lambda}$ is introduced:

$$\tilde{\Lambda}(q,\{\mathrm{S}(\mathbf{q})\}) = 32\pi^3 q^2\Lambda_0\,\mathrm{S}(\mathbf{q})\,, \tag{12}$$

Thus, the general form of the dynamic equation (11) for the virtual structure factor is the same as that of Cahn-Hilliard equation (4) but substitution of the structure factor $\mathrm{S}(q)$ for the order parameter $\delta\varphi$. In fact, both equations are special cases of general phenomenological approximation, according to which the rate of relaxation of an order parameter is linear with respect to the corresponding thermodynamic force defined as the derivative of the free energy with respect to the order parameter under consideration:

$$\partial x_i/\partial t = -\Lambda_{ij}(\{x_l\})X_j \tag{13}$$

When parameters x are small then the thermodynamic forces depend on x linearly, in which case eq. (13) is simply the linearized Onsager equation. In general case the thermodynamic forces are non-linear with respect to x, and then eq. (13) is an approximate but constructive way to describe non-linear relaxation in the system. Thus, the presented derivation enabled us not only to show that the dynamical equation for the virtual structure factor belongs, like the

Cahn-Hilliard equation, to the type (13), but also to obtain explicitly the corresponding effective kinetic coefficient (12).

However, two problems are left still unsolved: i) we neglected until now the existence of heat noise (dynamic fluctuations), and ii) we need an explicit expression for the thermodynamic force $\delta F/\delta \mathrm{S}(\mathbf{q})$. To solve these problems, we consider the thermodynamic (i.e. weighted over all fluctuations) free energy (1) and structure factor

$$\mathrm{S}(\mathbf{q}) = \int \mathrm{S}(\mathbf{q}) \exp[-F(\{\mathrm{S}(\mathbf{q})\})/T]\delta \mathrm{S}(\mathbf{q}) \Big/ \int \exp[-F(\{\mathrm{S}(\mathbf{q})\})/T]\delta \mathrm{S}(\mathbf{q}) \qquad (14)$$

As shown by field theoretical methods $^{5,6)}$, the free energy (1) can be represented as follows:

$$\mathrm{F} = \min_{\{G(\mathbf{x},t)\}} \widetilde{F}(T, \{\mathrm{G}(\mathbf{x},t)\}); \qquad (15)$$

where the functional $\widetilde{F}(T, \{\mathrm{G}(\mathbf{x},t)\}, \{\overline{\Phi}_i(\mathbf{r},t)\})$, that can be considered as the desired functional of generally non-uniform and non-equilibrium values of the thermodynamic correlation function and order parameter, has the following form:

$$\begin{aligned}\widetilde{F}(T, \{G(\mathbf{x},t)\})/T = {} & \int (\Gamma_{ij}^{(2)}(\mathbf{x}_1 - \mathbf{x}_2) - G_{ij}^{-1}(\mathbf{x}_1,\mathbf{x}_2)) G_{ji}(\mathbf{x}_1,\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 / 2 \\ & - \int Sp(\ln G(\mathbf{x}_1,\mathbf{x}_2) - \ln g(\mathbf{x}_1,\mathbf{x}_2)) d\mathbf{x}_1 d\mathbf{x}_2 / 2 \\ & - \sigma(\{\overline{\Phi}_i(\mathbf{r})\}, \{G(\mathbf{x}_1,\mathbf{x}_2)\}) + \int \overline{\Phi}_i(\mathbf{x}_1) \Gamma_{ij}^{(2)}(\mathbf{x}_1 - \mathbf{x}_2) \overline{\Phi}_j(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 / 2\end{aligned} \qquad (16)$$

functional $\sigma(\{\overline{\Phi}(\mathrm{r})\}, \{G(\mathbf{x}_1,\mathbf{x}_2)\})$ being the generating function of so-called 2-irreducible diagrams appearing in expansion of free energy (1) on powers of the parameters α and β. Assuming that i) the dynamic equation for the thermodynamic structure factor (14) is also of type (13) and ii) the averaged over all initial realisations value of the order parameter is zero, we get finally $^{7)}$

$$\partial \mathrm{S}(\mathbf{q})/\partial t = -T^{-1} \widetilde{\Lambda}(q, \{\mathrm{S}(\mathbf{q})\}) \, \delta \widetilde{F}/\delta \mathrm{S}(\mathbf{q}) \qquad (17)$$

Here the kinetic coefficient is defined by (12), since for large deviations from equilibrium the effects of heat noise should be negligible, and expression for the thermodynamic force follows $^{7)}$ from (16):

$$X(q) = \delta \widetilde{F}/\delta \mathrm{S}(\mathbf{q}) = -[\mathrm{S}^{-1}(q) - (\Gamma(q) - \Sigma)]/[2(2\pi)^3] \qquad (18)$$

$\Sigma(q, \{\mathrm{S}(\mathbf{p},t)\})$ being the corresponding mass operator. It follows from (18) that in the thermodynamic equilibrium, when $X=0$, the bare and renormalized correlation functions $\mathrm{S}(q)$ and $\Gamma^{-1}(q)$, respectively, are interrelated by the Dyson equation. In zero approximation $\Sigma=0$ and substituting (18) into (17) results into the Cook expression $^{2)}$ for the structure factor:

$$S_{Cook}(\mathbf{q},t) = (\Gamma(q))^{-1} + \left[(\Gamma_0(q))^{-1} - (\Gamma(q))^{-1}\right]\exp\left(-2q^2\,\Gamma(q)\,\Lambda_0\,t\right), \qquad (19)$$

with $\Gamma(q)$, $\Gamma_0(q)$ defined in (3). The function (19) has a sharp maximum at $q^2 = -\tau/2$.

Solution of Dynamic Equation for Structure Factor in One-Loop Approximation of Perturbation Theory

In this approximation $\Sigma(q,\{S(\mathbf{q},t)\}) = -(\beta/6)\int S(\mathbf{q})d\mathbf{q}/(2\pi)^3$ and eq. (18) takes the form

$$\partial S(\mathbf{q})/\partial t = -2\Lambda q^2 S(\mathbf{q})\left(\Gamma(\mathbf{q}) + (\beta/6)\int S(\mathbf{p})d\mathbf{p}/(2\pi)^3 - S^{-1}(\mathbf{q})\right) \qquad (20)$$

which is nothing but the equation derived by Langer [3)] on the base of rather different considerations. (Note, however, that taking into account the next terms of the free energy expansion leads to a difference between our general dynamic equation (11) and that of Langer.) In the vicinity of the peak of the scattering factor the term $S^{-1}(\mathbf{q})$ can be neglected. Then eq. (20) can be written as

$$\partial S(\mathbf{q})/\partial t = -2\Lambda_0 q^2 S(\mathbf{q})\left(\Gamma(\mathbf{q}) + (\beta/6)\int S(\mathbf{q}')\,d\mathbf{q}'/(2\pi)^3\right) \qquad (21)$$

Substituting expression (3) for $\Gamma(\mathbf{q})$ in (21) yields:

$$\partial S(\mathbf{q})/\partial t = -2\Lambda q^2(a^2q^2 + \tau)S(\mathbf{q},t) - (\beta/3)\Lambda\,q^2 S(\mathbf{q},t)\int S(\mathbf{q}',t)\,d\mathbf{q}'/(2\pi)^3 \qquad (22)$$

Let us introduce designation $W(t) = \int_0^t dt' \int S(\mathbf{q}',t')\,d\mathbf{q}'/(2\pi)^3$. Then eq. (22) can be written as

$$\partial S(\mathbf{q},t)/\partial t = -2\Lambda_0 q^2\left(a^2q^2 + \tau + (\beta/6)(dW/dt)\right)S(\mathbf{q},t) \qquad (24)$$

The solution of this differential equation is:

$$S(q,t) = S_0(q)\exp\left(-2\Lambda q^2\left((a^2q^2+\tau)t + (\beta/6)\,W(t)\right)\right), \qquad (25)$$

with $S_0(q) = S(q,0)$. Substituting solution (25) in the definition of $W(t)$ gives the differential first order equation

$$dW(t)/dt = \int_0^\infty q^2 S_0(q)\exp\left(-2\Lambda q^2\left((a^2q^2+\tau)t + (\beta/6)W(t)\right)\right)dq/\left(2\pi^2\right) \qquad (26)$$

Taking into account that the function $S_0(q)$ has maximum at $q = 0$, $|\tau| << \tau_0$, and the range of interest is that of small wave numbers q, we set approximately $S_0(q) = const$. So,

$$\frac{dW(t)}{dt} = \frac{S_0}{2\pi^2}\int_0^\infty q^2\exp\left(-2\Lambda a^2q^4t + 2\Lambda\left(|\tau|t - \frac{\beta}{6}W(t)\right)q^2\right)dq$$

With new notation $y^4 = 2\Lambda a^2 t q^4$, the expression for $dW(t)/dt$ takes the following form:

$$\frac{dW(t)}{dt} = \frac{S_0}{2\pi^2(2\Lambda a^2 t)^{3/4}} \int_0^\infty y^2 \exp\left(\xi y^2 - y^4\right) dy, \tag{27}$$

where

$$\xi = \frac{1}{a}\sqrt{\frac{2\Lambda}{t}}\left(|\tau| t - \frac{\beta}{6} W\right) \tag{28}$$

Let us consider set of functions $f_n(\xi) = \int_0^\infty y^n \exp(\xi y^2 - y^4) dy$. They can be expressed in terms of parabolic cylinder functions. In particular,

$$f_2(\xi) = e^{\xi^2/8} 2^{-7/4} \pi V\left(1, \frac{\xi}{\sqrt{2}}\right),$$

where parabolic cylinder function $V(a,x)$ [8)] (in our case $a = 1$) has the asymptotic (when $x \to \infty$) $V(a,x) \sim \sqrt{2/\pi}\, e^{x^2/4} x^{a-1/2}\left(1 + o\left(1/x\right)\right)$.

In terms of these functions, the differential equation for $W(t)$ takes the form

$$\frac{dW(t)}{dt} = \frac{S_0}{2\pi^2(2\Lambda a^2 t)^{3/4}} f_2(\xi), \tag{29}$$

Taking the derivative of somewhat modified expression (28) with respect to t yields:

$$\sqrt{\frac{a^2 t}{2\Lambda}}\left(\frac{1}{2t}\xi + \xi'\right) = |\tau| - \frac{\beta}{6} W' \tag{30}$$

and substituting expression (29) for dW/dt into (30) gives finally:

$$\frac{1}{2t}\xi + \xi' - \sqrt{\frac{2\Lambda}{a^2 t}}\left(|\tau| - \frac{\beta}{6}\frac{G_0}{2\pi^2\left(2\Lambda a^2 t\right)^{3/4}} f_2(\xi)\right) = 0.$$

Notice now, that the strong inequality $\frac{1}{2t}\xi + \xi' \ll \sqrt{\frac{2\Lambda}{a^2 t}}\left(|\tau| - \frac{\beta}{6}\frac{S_0}{2\pi^2\left(2\Lambda a^2 t\right)^{3/4}} f_2(\xi)\right)$ holds since $f_2(\xi)$ increases very rapidly. Therefore, for large ξ_0 we set approximately

$$\frac{1}{2t}\xi_0 + \xi_0' = 0, \quad \sqrt{\frac{2\Lambda}{a^2 t}}\left(|\tau| - \frac{\beta}{6}\frac{S_0}{2\pi^2\left(2\Lambda a^2 t\right)^{3/4}} f_2(\xi_0)\right) \to 0$$

Thus, we have $f_2(\xi_0) \sim C_1 t^{3/4}$. On the other hand, $f_2(\xi_0) \sim C e^{\xi_0^2/4} \xi_0^{1/2}$ for large ξ_0 (with $C = 2^{-3/2}\sqrt{\pi}$) which yields

$$\ln C+\xi_0^2/4+\frac{1}{2}\ln\xi_0=\ln C_1+\frac{3}{4}\ln t \tag{31}$$

In the case of large ξ_0 the term $\xi_0^2/4$ is substantially larger than other terms and, therefore, it is the main term of asymptotic. It follows from (31) in the first approximation $\xi_0^2\sim 3\ln t$. Substituting it back in (31) we get in the next approximation $\xi_0^2\sim 3\ln t-\ln(3\ln t)$. Using the expression (28) we can write as $\sqrt{2\Lambda/(a^2t)}\left(|\tau|t-(\beta/6)W\right)\approx\sqrt{3\ln t-\ln(3\ln t)}$. For large times the term $\ln(3\ln t)$ may be disregarded and we get finally

$$(\beta/6)W\approx|\tau|t-\sqrt{3a^2t\ln t/(2\Lambda)}. \tag{32}$$

If we substitute the expression (32) in formula (25) and uncover inner parentheses then the expression for the structure factor will be equal:

$$\mathrm{S}(\mathbf{q},t)=\mathrm{S}_0(\mathbf{q})\exp\left(-2\Lambda a^2q^4t+\sqrt{6\Lambda a^2q^4t\ln t}\right) \tag{33}$$

The function $h(q)=-2\Lambda a^2q^4t+\sqrt{6\Lambda a^2q^4t\ln t}$ has maximum at the point

$$Q_{\max}=\left(3\ln t/\left(8\Lambda a^2t\right)\right)^{1/4}. \tag{34}$$

Therefore, taking into account that $\mathrm{S}_0(Q_{\max})\approx\mathrm{S}_0(0)$ (since $q_m\to 0$ at $t\to\infty$) we get for the maximum of the structure factor the following expression:

$$\mathrm{S}(Q_{\max},t)=\mathrm{S}_0(0)\exp\left(-2\Lambda a^2Q_{\max}^4\ t+\sqrt{6\Lambda a^2Q_{\max}^4t\ln t}\right)=\mathrm{S}_0(0)\,t^{3/4}. \tag{35}$$

Thus, the peak value of the structure factor grows as power function of time. Eqs. (33)-(35) provide the asymptotic behaviour of structure function without further corrections for ξ_0.

The numerically calculated, using expression (29), peak value $\mathrm{S}_{\max}(t)=\mathrm{S}(Q_{\max},t)$ and location of the maximum $Q_{\max}(t)$ are plotted at Figs. 1, 2 at different supercoolings τ. For convenience, the plots are built in reduced variables $Q_{\max}\to 2Q_{\max}/|\tau|^{1/2}$ and $t\to t\tau^2/2$.

As seen from Fig. 2, the characteristic grain size L grows at large times, up to logarithmic corrections, in agreement with the results of ref. [9], as follows: $L\propto 2\pi/Q_{\max}\sim t^{1/4}$.

In turn, the peak value of the structure factor grows at large times as consistent with the asymptotic expression (35), i.e. $S_{\max}\sim t^{3/4}$.

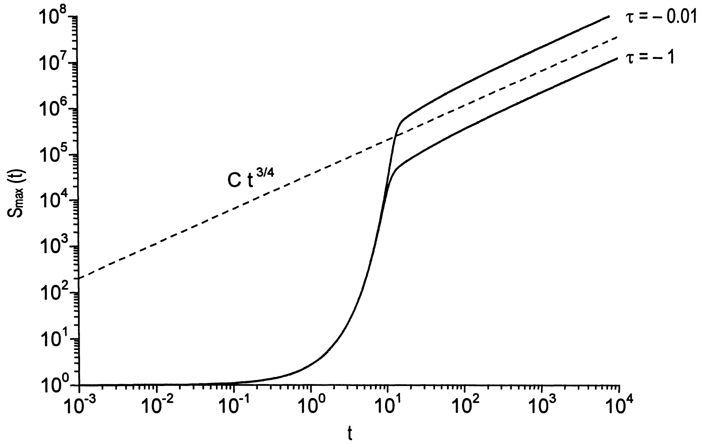

Fig. 1. Plot of function $S(Q_{max}, t)$ vs t in logarithmic scale (the result of the numerical solution of the equation (29)), for different values of temperature τ (solid lines) and the asymptotic (the expression (35)) (dotted line).

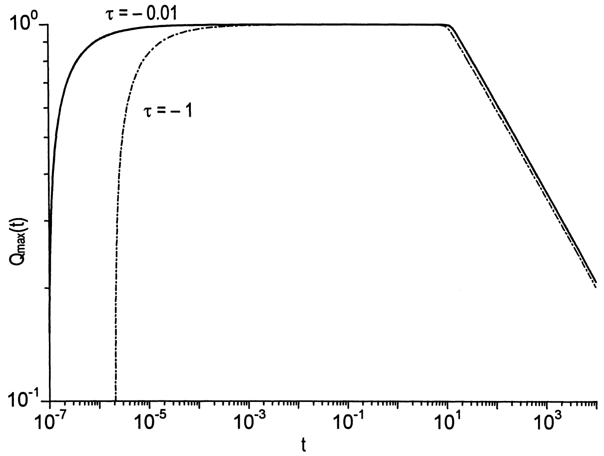

Fig. 2. Plot of function $\log Q_{max}(t)$ vs $\log t$, (the expression (34)), for different values of temperature τ ($\tau = -0.01$ – solid line, $\tau = -1$ – dotted line).

One should emphasise that these values of the characteristic exponents are directly related to the approximation we have used. Thus, the results obtained correspond to an intermediate asymptotic valid for large but not extremely large times. To describe the asymptotic behaviour of the quantities of interest at such extremely large times we should go beyond the Hartree approximation and take into account the higher diagrams appearing in the mass operator $\Sigma(q, \{S(\mathbf{p}, t)\})$ in formula (18).

Conclusion

We presented a new derivation of the dynamic equation for the structure factor, whose first approximation for the systems with scalar order parameter is identical to the famous Langer equation $^{3)}$. However, our approach is more general. In particular, it enables one to consider i) the systems with multi-component order parameter (e.g., solution of a few of polymer component in a solvent), ii) the situations with time and space dependent environment (e.g., spinodal decomposition under solvent evaporation), and iii) still later stages of the spinodal decomposition to be described beyond the first-order (Hartree) approximation. We consider these generalisations elsewhere.

E.P. acknowledges financial support by INTAS (award YSF99-4042).

References

1. J.W. Cahn, J.E. Hilliard, *J. Chem. Phys.*, **28**, 258 (1958)
2. H.E. Cook, *Acta Metall.*, **18**, 297 (1970)
3. J.S. Langer, M. Bar-on, H.D. Miller, *Phys. Rev. A*, **11**, 1417 (1975)
4. E.V.Prostomolotova, I.Ya. Erukhimovich and L.I.Manevich, *Polymer Science*, *Ser.A*, **39** (6), 1014 (1997)
5. C.J. de Dominicis, *Math.Phys.*, **3**, 983 (1962)
6. A.V. Dobrynin, I.Ya. Erukhimovich, *J. Phys. II*, **1**, 1387 (1991)
7. I.Ya. Erukhimovich, E.V. Prostomolotova, *JETP Letters*, **66** (6), 463 (1997)
8. *Handbook of Mathematical Functions*, M. Abramowitz and I.A. Stegun (Eds.), Dover, New York 1965.
9. C. Castellano, F. Corberi, *Phys. Rev. E.*, **57,** No.1, 672 (1998).