Time-Dependent Ginzburg-Landau Equation for an N-Component Model of Self-Assembled Fluids.

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Abstract. – We study the time evolution of an N-component model of bicontinuous microemulsions based on a time-dependent Ginzburg-Landau (GL) equation quenched from a high-temperature uncorrelated state to the low-temperature phases. The behaviour of the dynamical structure factor $C(k, t)$ is obtained, in each phase, in the framework of the large-N limit with both conserved (COP) and non-conserved (NCOP) order parameter dynamics. At zero temperature the system shows multiscaling in the unstructured region up to the tricritical point for the COP, whereas ordinary scaling is obeyed for NCOP. In the structured phase, instead, the conservation law is found to be irrelevant and the form $C(k, t) \sim t^{|x|/z} f(|k - k_m| t^{1/2})$, with $x = 1$ and $z = 2$, is obtained in every case. Simple scaling relations are also derived for the structure factor as a function of the final temperature of the thermal bath.

Self-assembled fluids are mixtures of water, oil and surfactants displaying a richer thermodynamic behaviour than ordinary fluids because they appear to have a tendency to order and form patterns. In fact, if the surface tension can be made sufficiently low, by increasing the surfactant concentration, one observes a microemulsion phase stabilized by spontaneous curvature and entropy of mixing, whereas at higher values of the surface tension one obtains oil-rich or water-rich regions. By further increasing the surfactant concentration, however, the fluid acquires an internal order as revealed by the several structured phases.

So far most of the experimental and theoretical studies have been devoted to the investigation of the equilibrium properties of such systems, whereas the properties far from equilibrium of complex fluids are not so well understood[1]. In the present letter we generalize to a large number of components the GL model proposed by Gompper-Schick[2, 3]
by writing the following Hamiltonian:

$$H[\phi(x)] = \int dx \left[ \frac{1}{2} (\nabla^2 \phi)^2 + \frac{b}{2} (\nabla \phi)^2 + \frac{w}{2N} (\phi)^2 (\nabla \phi)^2 + \frac{r}{2} (\phi)^2 + \frac{g}{4N} ((\phi)^2)^2 \right], \quad (1)$$

where $r$ and $g$ (with $g > 0$) are the quadratic and quartic couplings of the GL theory. The term containing the squared Laplacian represents a curvature energy contribution, whereas the second and the third terms are proportional to the surface energy. The peculiarity of the self-assembled fluids is reflected by the presence of higher-order derivatives in the gradient expansion and by the sign of the coefficient $b$, as found from the fits of the experimental data [4], while $w > 0$.

Incidentally, our results turn out to be of interest for a classical problem of relaxation dynamics, apparently quite different as the hydrodynamic fluctuation at the convective instability, the so-called Swift-Hohenberg model [5-8].

Within the large-$N$ limit the equation of motion for the order parameter and its fluctuations can be written in a closed form [9-11]. We associate the modulus of the vector order parameter $\phi(x, t) = (\phi_1(x, t), \ldots, \phi_N(x, t))$ with the difference in the density of water and oil molecules. The evolution towards equilibrium is described by the Langevin equation

$$\frac{\partial \phi_a(x, t)}{\partial t} = -\Gamma(x) \frac{\delta}{\partial \phi_a(x, t)} H[\phi(x)] + \eta_a(x, t). \quad (2)$$

Here $\eta(x, t)$ represents a Gaussian white noise with zero average and $\langle \eta_a(x, t) \eta_{\beta}(x', t') \rangle = 2T_f \Gamma(x) \delta_{a, \beta} \delta(x - x') \delta(t - t')$, where $T_f$ is the temperature of the final equilibrium state and the kinetic coefficient takes a constant value $\Gamma$ for non-conserved order parameter (NCOP), whereas it is given by $-\Gamma \nabla^2$ in the conserved case (COP).

We consider the long-range behaviour of the equal-time real space connected correlation function $C(r, t) = \langle \phi_a(R + r, t) \phi_a(R, t) \rangle$ and its Fourier transform, the structure factor, $\tilde{C}(k, t)$, which are both independent of the index $a$ due to the internal symmetry.

In the large-$N$ limit from eq. (2) one obtains

$$\frac{d}{dt} \tilde{C}(k, t) = -2k^p \Gamma k^4 + \dot{B}(t) k^2 + \dot{Q}(t) \tilde{C}(k, t) + 2k^p \Gamma T_f, \quad (3)$$

with $p = 0$ for NCOP dynamics and $p = 2$ for COP. We have introduced the two auxiliary functions $\dot{B}(t)$ and $\dot{Q}(t)$, which have to be determined self-consistently through

$$\dot{B}(t) = b + wS_0(t), \quad (4)$$

$$\dot{Q}(t) = r + gS_0(t) + wS_2(t), \quad (5)$$

where the integrals

$$S_n(t) = \int_{|k| < \Lambda} \frac{d^d k}{(2\pi)^d} \tilde{C}(k, t) k^n, \quad (6)$$

with $n = 0, 2$, contain a phenomenological momentum cut-off $\Lambda$.

At equilibrium (see also [12]), when $r \leq 0$, the system displays a low-temperature ordered, «magnetic» phase with non-vanishing order parameter $\langle \phi \rangle$ and a high-temperature...
Fig. 1. – Phase diagram for $r \leq 0$ and $d = 3$.

disordered (paramagnetic) phase as shown in fig. 1. In order to draw the phase diagram of the system, we consider the equilibrium value of the structure factor $\bar{C}_{eq}(k)$ which reads

$$\bar{C}_{eq}(k) = \frac{T_f}{k^4 + b_r k^2 + D},$$

where $b_r = \lim_{t \to \infty} (b + wS_0(t))$ and $D = \lim_{t \to \infty} (r + gS_0(t) + wS_2(t))$. The «ordered phase» $\langle \phi \neq 0 \rangle$ is bounded from above by the line of «magnetic» critical points $T_c(b)$ shown in fig. 1. It terminates at the tricritical point $(b_L = w/g, T_{tr})$, located at $T_{tr} = 0$ in $d < 4$. Points below such a curve correspond to a vanishing value of the parameter $D$. In other words the line $T_c(b)$ separates a high-temperature phase with finite correlation length and finite fluctuations from a low-temperature magnetic phase with infinite correlation length and divergent fluctuations at zero wave vector, due to the presence of massless Goldstone modes.

Within the disordered phase the two-particle correlation function displays two different behaviours according to the sign of the discrimination $\Delta = [D - b_r^2 / 4]$. In fact, the vanishing of $\Delta$ identifies the so-called disorder line, i.e. the borderline between a regime (since it is not a proper thermodynamic phase) with monotonically decaying correlations, which is the analogue of a paramagnetic phase, and a phase with oscillatory-decaying correlations, which in the present model corresponds to a microemulsion phase. The locus where the structure factor, $\bar{C}_{eq}(k)$, starts developing a peak at finite wave vector $k$, when $b_r(T_f) = 0$, is named Lifshitz line. It is contained in the microemulsion phase and terminates at the tricritical point. To summarize, for positive values of $\Delta$, $C(r) \sim \exp[-r/\bar{\xi}] \sin(k_m r)$, with $1/\bar{\xi} = [(1/2) \sqrt{D + b_r/4}]^{1/2}$ and with $k_m = [(1/2) \sqrt{D - b_r/4}]^{1/2}$. For negative values of $\Delta$, the correlation decays monotonically, showing an Ornstein-Zernike behaviour. Finally along the semiaxes $T_f = 0$ and $b \leq r w/g$, $\Delta = 0$ and the structure factor diverges at a finite wave vector. Such a line is the remnant of the lamellar phase, which is unstable for any finite temperature, because the system does not support topological defects in any dimension $d$ less than $N$.

We shall consider now the phase ordering of the present system following a quench from
an uncorrelated high-temperature state for different choices of \( b_r \). We assume the initial state to be uncorrelated and choose the initial condition \( C(k, 0) = \Delta_0 = \text{const.} \) In the following we shall consider \( r < 0 \). The asymptotic form of \( \widetilde{C}(k, t) \), for the \( T_f = 0 \) case can be easily calculated by imposing the matching of \( S_0(t) \) and \( S_2(t) \), obtained by means of eq. (8) with their equilibrium constant values.

For NCOP and positive \( b_r \), since the curvature term is asymptotically irrelevant, the structure factor has the usual scaling form as for simple fluids, \( \widetilde{C}(k, t) \sim t^{z/2} f(kt^{1/2}) \), with \( f(x) = \exp(-x^2) \), \( z = d \) and \( z = 2 \), for a quench at \( T_f < T_s \). The exponent \( z = 2 \) is, in fact, related to the growth of the domain size \( L(t) = (2Tt)^{1/2} \), which is controlled by surface tension. For COP one observes, instead, the multiscaling behaviour of the structure factor [9], due to the existence of two marginally different scaling lengths, \( L(t) = (2Tt)^{1/4} \) and \( k_m^{-1}(t) \sim (t/\log t)^{1/4} \), where \( k_m(t) \) is the position of the peak of the structure factor \( \widetilde{C}(k, t) \). This results in a multiscaling form for \( \widetilde{C}(k, t) \sim \left(k_m^{2-d} L^{2}\phi(k/k_m)\right) \), with \( \phi(x) = 1 - (1 - x^2)^2 \).

Of particular interest is the quench at the tricritical point \( (b_r = 0, T_f = 0) \), i.e. in correspondence of the bare value \( b_L = m\nu/g \), where the «magnetic», the «paramagnetic» and the «lamellar» phases meet.

We study, first, the growth of the structure factor upon approaching \( T_f = 0 \) along a particular Lifshitz line, by considering the simpler case \( w = 0 \), which yields \( b_L = 0 \). For the NCOP at \( T_f = 0 \) the electron factor reads \( C(k, t) = \Delta_0 \exp(-2T^{k_4} t^{1/4}) \), i.e. a scaling form characterized by \( z = d \), \( z = 4 \) and scaling function \( f(x) = \exp(-x^2) \). The typical domain size evolves according to \( L(t) = (2Tt)^{1/4} \), being controlled by the curvature rigidity and not by surface tension. For the same choice of parameters in the COP case, instead, the growth process depends on two distinct lengths \( L(t) = (2Tt)^{1/6} \) and \( k_m^{-1}(t) \), where \( k_m(t) \) is the wave vector where \( C(k, t) \) reaches its maximum and varies in time as \( k_m(t) \sim ((d \ln t)/t)^{1/6} \). The same mechanism which determines the multiscaling behaviour of the structure factor upon approaching an ordinary critical point leads to the multiscaling form for \( \widetilde{C}(k, t) \sim \left(k_m^{2-d} L^{2}\phi(k/k_m)\right) \), with \( \phi(x) = (3x^2 - x^6)/2 \).

For the choice \( b = 0, w = 0 \) and \( T_f > 0 \) we have investigated numerically the behaviour of the solutions of eq. (3), with NCOP. As shown in fig. 2 by plotting \( C(k_m, t) \) times \( T_f^{d/4-d} \).

Fig. 2. – Data collapse for the peak of the structure factor at different temperatures \( (T_f = 0.1, 0.05, 0.01, 0.005, 0.001) \) for \( d = 3, b = 0, r = -0.1, g = 1, w = 0 \).
against time multiplied by $T_t^{d/(4-d)}$, one obtains a remarkable data collapse over several decades. This suggests the existence of a typical relaxation time $\tau$ which scales with the temperature $T_t$ according to the law $\tau \sim T_t^{-d/(4-d)}$. Such a dynamic-scaling relation can be deduced heuristically, by matching the typical value of the maximum of the structure factor, which grows as $\tilde{C}(k, t) \sim t^{d/4}$ up to the characteristic time $\tau$, with the equilibrium value $G_{eq}(k_m)$ at $T_t$ which is proportional to $T_t^{-d/(4-d)}$.

Let us consider a slightly different case, where $b = rv/g$, i.e. a quench to the tricritical point at $(b = 0, T_t = 0)$. Here the two lengths $k_m^{-1}$ and $\xi$, discussed above, diverge upon approaching equilibrium. One observes a crossover from an initial regime characterized by a structure factor with a peak at finite values of $k$ to the true asymptotic regime displaying the ordinary Bragg peak at $k = 0$ at late times. For NCOP, one finds from the self-consistency conditions eqs. (4) and (5) that asymptotically $2\Gamma B(t) - at^{1/2}$, with $a > 0$, and $2\Gamma Q(t) = -d \log(t)/4$. Therefore the structure factor assumes at late times the scaling form $\tilde{C}(k, t) \sim t^{d/4} \exp[-ax^4 + 2ax^2]$, where $x = (2\Gamma t)^{1/4}k$. Notice the unusual feature, for NCOP, of the maximum of the structure factor at finite wave vector moving slowly at the rate $\sim t^{-1/4}$ towards the origin. In other words, initially $B(t) < 0$ (for times such that $S_0(t) < \mid b \mid/w$), and the system promotes fluctuations with $k_m(t) > 0$, which are eventually suppressed by the growing of correlations which cause $k_m \to 0$. However, the two characteristic lengths $L(t)$ and $k_m^{-1}(t)$ vanish at the same rate and standard scaling is observed.

Upon crossing the Lifshitz line and $b_r < 0$ the asymptotic structure factor $C(k, t)$ displays a peak at finite wave vector, at position $k_m(t) = \sqrt{-B(t)/2t}$. The main difference with the cases treated above is the finite value of $k_m^{-1}$ in the late regime.

For the NCOP dynamics at $T_t = 0$ a saddle-point estimate of the integrals yields

$$S_n(t) \sim K_4 \exp[-2\Gamma Q(t)] \exp \left[ \frac{\Gamma B^2(t)}{2t} \right] \left[ \frac{-B(t)}{2t} \right]^{(d-1+n)/2} \left[ -B(t) \right]^{-1/2},$$

with $K_4 = \left[ 2^{d-1} \pi^{d/2} \Gamma(d/2) \right]^{-1}$. Upon requiring that $S_0(t)$ and $S_2(t)$ reach a constant value at equilibrium, we obtain

$$Q(t) \sim \frac{B^2(t)}{4t} - \frac{1}{4\Gamma} \log[-B(t)] + \frac{(d - 1)}{4\Gamma} \log \left[ -\frac{B(t)}{2t} \right].$$

For consistency, since in this region for large times $\dot{B}(t) < 0$ and $S_2(t)/S_0(t) \to k_m^2$, we find asymptotically $B(t) \sim -2k_m^2t$. The structure factor develops a peak at finite values of $k$, corresponding to a quasi-ordered pattern, with periodicity given by $2\pi/k_m$. The height of the peak grows in time according to the power law $t^{1/2}$. This is due to the competition between curvature and surface-tension-controlled fluctuations which eventually lead to a layered structure at $T_t = 0$. Within this regime we find the following asymptotic form of the structure factor:

$$C(k, t) \sim \sqrt{t} \exp \left[ -2\Gamma \left( k^2 + \frac{B(t)}{2t} \right)^2 t \right],$$

which obeys the scaling form $C(k, t) \sim t^{z/2} f(k - k_m | t^{1/2})$, with $z = 1$ and $z = 2$. This unusual lack of dependence of the structure factor on the dimensionality, $d$, reflects the fact that the largest fluctuations characterizing the ordering process have a finite wave number and thus the density-of-state contribution does not manifest itself. We have considered also the finite-temperature behaviour of eq. (3) and found data collapse for the curves representing
the height of the peak times $T_t$ vs. the time multiplied by $T_t^2$. In fact, the height of the peak grows according to eq. (10) as $t^{1/2}$, while for $T_t > 0$ a simple calculation shows that the structure factor settles at a finite value $\tilde{C}_{eq}(k_m) \sim T_t^{-1}$. The matching gives a relaxation time $\tau$ proportional to $T_t^{-2}$.

For COP the only qualitative difference observed is the weak dependence of the peak position on time, since $k_m(t)$ approaches as $\log(t)/t$ its equilibrium value. In this case, therefore, the conservation law turns out to be an irrelevant constraint since it acts at $k = 0$, while the most important fluctuations are grown at finite $k$.

A natural question is to ask ourselves how generic is the $t^{1/2}$ behaviour we have observed, namely whether the present results for $N \to \infty$ have any relevance with respect to other models. We believe that our findings are consistent with the very late time behaviour ($z = 2$) observed in numerical simulations by Elder et al. [7] in a study of the NCOP Swift-Hohenberg equation with $N = 1$ and $d = 2$ within the structured phase. On the other hand, apart from a special choice of parameters, we do not find any evidence in our model of their growth exponent $z = 4$ related to curvature relaxation, a feature probably due to the lack of topological defects. We finally remark that the equations we solved are very closely related to the dynamical Hartree approximation for $N = 1$ [1].

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