Harmonic Corrections near the Ordering Transition

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Harmonic Corrections near the Ordering Transition.

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Abstract. – We study the role played by harmonic corrections to the order parameter in the Landau-Ginzburg description of the transition from an isotropic to a weakly ordered state, and find two further stable structures in the phase diagram (face-centred cubic and square) in addition to the usual three crystalline phases (body-centred cubic, hexagonal and lamellar) predicted by the standard analysis. This enlarges the range of validity of the theory and gives a quantitative criterion for the possibility of formation of a face-centred cubic phase near the liquid-solid coexistence line.

The formation of long-range ordered structures from a high-temperature isotropic phase is a well known but still controversial problem in phase transitions [1, 2]. When the transition is second-order or weakly first-order the Landau-Ginzburg formalism provides a convenient framework for its discussion. It is thus specially adequate for the description of ordering transitions to mesoscopic periodic structures with modulations on a length scale of $(5 \div 500)$ nm. The formalism has been applied to a large variety of systems, including diblock copolymers [3, 4], microemulsions [5-7] and other surfactant systems [8-11], colloidal crystals [12, 13] and Benard convective instabilities [14]. More generally it has been used to discuss the stable crystalline structures expected near the solid-liquid transition line of simple elements [15] and the stability of quasi-crystalline phases [16].

One severe drawback of the standard formulation of the Landau-Ginzburg theory is that it only predicts the formation of three different crystalline lattices: body-centred cubic (BCC), the two-dimensional hexagonal (H) and the one-dimensional lamellar (L). Real systems are known to form a much wider variety of structures, ranging from the two-dimensional square lattice (S) [17], simple cubic (SC) [18] or face-centred cubic phases (FCC) [13] to more exotic spatial organizations such the «double-diamond» phase [19] of block copolymers. We point out in this letter that such a restricted phase diagram is partly a consequence of the «first-harmonic approximation» for the order parameter, by which we mean a restriction of nonzero-order parameter amplitudes to a minimal set of reciprocal lattice vectors for each structure considered. We show explicitly, within the mean-field

theory, how an extension of the model to include «harmonic corrections» (finite amplitudes at nonminimal reciprocal lattice vectors) can lead to new structures in the phase diagram (1).

Our starting point [2, 20] is as usual the Landau-Ginzburg expansion of the free-energy density as a function of the order parameter ψ

$$F[\psi_q] = \frac{1}{2!}\int_q S^{-1}(q)\,\psi_q\psi_{-q} + \frac{\mu}{3!}\int_q\int_{q'}\psi_q\psi_{q'}\psi_{-q-q'} + \frac{\lambda}{4!}\int_q\int_{q'}\int_{q''}\psi_q\psi_{q'}\psi_{q''}\psi_{-q-q'-q''}, \tag{1}$$

where $S(q = |\boldsymbol{q}|)$ is the Fourier transform of the two-point correlation function in the disordered homogeneous phase. The order parameter is chosen to vanish on average in the liquid and has a nonzero value in the ordered phases. The third-order coefficient μ is a measure of the intrinsic asymmetry between positive and negative values of ψ, it is zero for completely symmetric systems and can, without loss of generality, be presumed positive otherwise. The fourth-order coefficient λ is always assumed positive for stability. In practice there are, for small μ, strong fluctuation effects which can be treated by applying a Hartree factorization to the λ term [21]. However in the present study of harmonic contributions we consider only, for simplicity, the mean-field theory.

In order to describe a particular crystalline structure, we first expand the order parameter in its Fourier components

$$\psi(\boldsymbol{r}) = \sum_{\{q_j\}} \psi_{q_j} \exp[i\boldsymbol{q}_j \cdot \boldsymbol{r}], \tag{2}$$

where the sum is over all the vectors of the corresponding reciprocal lattice. In the standard description of the transition one truncates the sum in eq. (2) at the nearest-neighbour shell ($|\boldsymbol{q}_j| = q_1$) and argues that this is a good enough approximation for the calculation of the free energy because, close to the transition, the susceptibility $S(q)$ is very sharply peaked around q_1. Inserting eq. (2) in the Landau-Ginzburg functional (1) gives then, for each investigated structure ς = BCC, H, L, S, FCC ..., a mean-field free energy of the form

$$F_\varsigma = A_\varsigma \tau\psi_\varsigma^2 + B_\varsigma \mu\psi_\varsigma^3 + C_\varsigma \lambda\psi_\varsigma^4 \tag{3}$$

with a single order-parameter ψ_ς. Here the «temperaturelike» control parameter τ is given by $\tau = S^{-1}(q_1)$ and the numerical coefficients A_ς, B_ς, C_ς depend on the number of ways in which the different reciprocal lattice vectors of the first-neighbours shell can combine to form, respectively, two-, three- and four-vector loops [15]. The complete phase diagram is then obtained by minimization of the free energies (3) with respect to the amplitudes ψ_ς and comparison of the values for different structures ς at the respective minima. This phase diagram may be displayed in a convenient way in the $[\tau/\lambda, \mu/\lambda]$-plane (fig. 1). For symmetric systems ($\mu = 0$) there is a second-order phase transition on decreasing temperature from the isotropic to the lamellar phase at $\tau = 0$. For asymmetric systems ($\mu \neq 0$) the transitions are first order. Under cooling the body-centred cubic phase appears first, at temperatures given by [3] $\tau = 0.119\mu^2/\lambda$ and then the hexagonal phase at $\tau = -0.0734\mu^2/\lambda$. The H-L transition takes place at $\tau = -2.87\mu^2/\lambda$.

The above treatment becomes exact (within mean-field theory) if $S(q)$ is vanishingly small for all q other than on the shell $q = q_1$ in reciprocal space. In practice the susceptibility has a finite width; hence even near a second-order transition there is a finite contribution to the Landau-Ginzburg free energy from Fourier components with $q > q_1$. These are the «harmonic corrections» whose effects we wish to study. In general the quadratic part of the

(1) A related approach has been first used by Troian and Mermin [16] who introduced an *ad-hoc* quadratic correction to the free energy in order to discuss the stability of the quasi-crystalline structure.

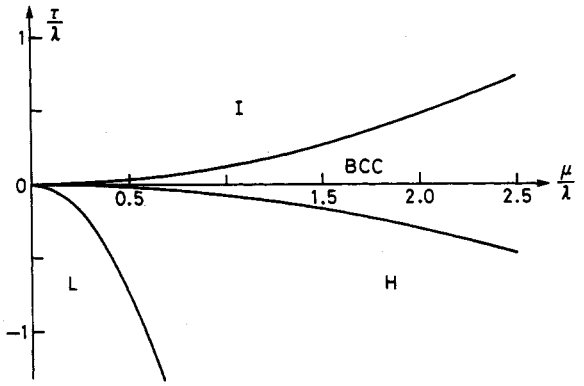

Fig. 1. – Mean-field phase diagram for the ordering transition calculated with a minimal set of reciprocal lattice vectors for each structure considered. Within this approximation only the isotropic (I), body-centred cubic (BCC), hexagonal (H) and lamellar (L) structures are present in the phase diagram.

correction term can be written as

$$F_2 = \frac{1}{2}\sum_i n_i S^{-1}(q_i)\,\psi_i^2\,, \tag{4}$$

where the sum runs over all the shells of successive neighbours, n_i is the number of neighbours in the i-th shell and ψ_i the i-th component of the order parameter. Similarly the third- and fourth-order terms of eq. (1) give, for each structure and each component ψ_i, a third- and fourth-order contribution to the free energy. There are also cross terms arising from the possible mixtures of different vectors from different shells, which add up to form three and four vector loops.

By comparison of the radius q_i of the successive reciprocal shells i, for the usual crystallographic structures (see table I), one can see that the correction to the free energy

TABLE I. – *Number of neighbours (n) and distances ($d = q/q_1$) of the consecutive shells of the reciprocal lattices for the most usual crystallographic structures.*

	L		S		H		SC		BCC		FCC	
	n	d	n	d	n	d	n	d	n	d	n	d
1st shell	2	1	4	1	6	1	6	1	12	1	8	1
2nd shell	2	2	4	$\sqrt{2}$	6	$\sqrt{3}$	12	$\sqrt{2}$	6	$\sqrt{2}$	6	$\sqrt{4/3}$
3rd shell	2	3	4	2	6	2	2	$\sqrt{3}$	24	$\sqrt{3}$	12	$\sqrt{8/3}$

which first comes into play on increasing values of q, arises from the second FCC shell at $q = \sqrt{4/3}q_1$. Next, there are contributions to the S, SC and BCC structures at $q = \sqrt{2}q_1$ followed by the third shell of the FCC at $q = \sqrt{8/3}q_1$. All the other harmonic contributions of the considered structures arise at higher q values. It is then possible to analyse the effect of the second-harmonic corrections to the free energy by chosing for the upper cut-off of eq. (4), the $q = \sqrt{2}q_1$ shell. This will provide the free energies of the FCC, S, SC and BCC structures with a second-order parameter while the hexagonal and lamellar free energies will remain with a single-order parameter. As discussed below, this choice of upper cut-off gives a correct account for the first nontrivial changes to the phase diagram introduced by the harmonic corrections in the mean-field approximation. The free energies for the

different structures can thus be written as

$$
\begin{cases}
\text{Lamellar:} \\
F = \tau\psi^2 + \frac{\lambda}{4}\psi^4 . \\
\text{Square:} \\
F = 2\tau\psi^2 + 2(\tau+\alpha)\phi^2 + 4\mu\psi^2\phi + \frac{3\lambda}{2}(\psi^4 + 4\psi^2\phi^2 + \phi^4) . \\
\text{Hexagonal:} \\
F = 3\tau\psi^2 + 2\mu\psi^3 + \frac{15\lambda}{4}\psi^4 . \\
\text{Simple cubic:} \\
F = 3\tau\psi^2 + 6(\tau+\alpha)\phi^2 + 12\mu\psi^2\phi + 8\mu\phi^3 + \frac{\lambda}{4}(15\psi^4 + 192\psi^2\phi^2 + 90\phi^4) . \\
\text{Body-centred cubic:} \\
F = 6\tau\psi^2 + 3(\tau+\alpha)\phi^2 + 12\mu\psi^2\phi + 8\mu\phi^3 + \frac{\lambda}{4}(90\psi^4 + 96\psi^2\phi^2 + 96\psi^3\phi + 15\phi^4) . \\
\text{Face-centred cubic:} \\
F = 4\tau\psi^2 + 3(\tau+\beta)\phi^2 + 12\mu\psi^2\phi + \frac{\lambda}{4}(36\psi^4 + 96\psi^2\phi^2 + 15\phi^4) .
\end{cases}
\tag{5}
$$

Here ψ, ϕ stand for the order parameter amplitudes in the first and second shells, respectively, and the coefficients α, β are defined by $\tau+\beta = S^{-1}(\sqrt{4/3}q_1)$; $\tau+\alpha = S^{-1}(\sqrt{2}q_1)$. Minimization of eqs. (5) and comparison of their values at the minimum determine the phase diagram which can be conveniently displayed in the $[\tau/\alpha, \mu/(\alpha\lambda)^{1/2}]$ space for each value of β. We find in this phase diagram (for all β) a region where the square phase is stable, the BCC-H-S triple point being situated at $\tau = -0.862\alpha$, $\mu = 2.112(\alpha\lambda)^{1/2}$. It is then clear that neglecting the harmonic contribution corresponds to setting $\alpha = \infty$ in which case the square phase is relegated to infinite values of the temperature and asymmetry. This new phase appears, within mean-field theory, purely as a result of the harmonic corrections.

The stability of the face-centred cubic structure depends on the ratio $\bar{\beta} = \beta/\alpha$ and thus on the exact shape of $S(q)$ (fig. 2 shows the phase diagram for $\beta = 0.01$). For $\bar{\beta} > 0.0435$ the FCC is never stable in the phase diagram, which corresponds to the case where the function $S(q)$ does not fall fast enough in between the FCC and BCC second-harmonic shells (respectively, $q_2 = \sqrt{4/3}q_1$ and $q_2 = \sqrt{2}q_1$). For $\bar{\beta} < 0.0435$ the FCC phase always exists at intermediate values of the asymmetry. Notice that a parabolic approximation to $S(q)^{-1}$ near $q = q_1$ (given by $S(q)^{-1} = \tau + (q-q_1)^2$) always yields $\bar{\beta} = 0.139$, a value too large to lead to an FCC phase. This is interesting because many improved treatments [21, 22] of the Landau-Ginzburg free energy are based on this form for $S(q)^{-1}$. Although valid close to the spinodal line, such a form may accidentally rule out certain structures, when second harmonics are included. It is also important to stress that $S(q)$ do not always fall monotonically from its maximum at q_1: it is clear for instance that in the case where the susceptibility presents a second maximum, a quadratic extrapolation will strongly underestimate the contribution from the harmonics close to the second peak.

We conclude with a remark on the accuracy of the second-harmonic approximation. It is

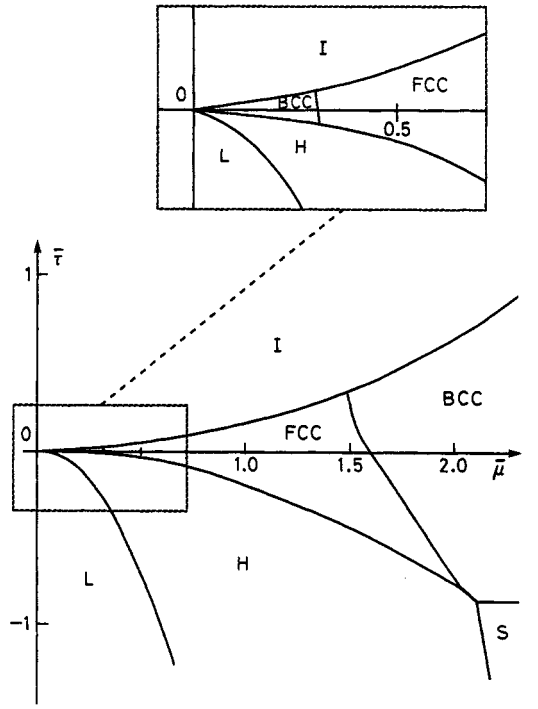

Fig. 2. – Mean-field phase diagram for the ordering transition calculated within the second-harmonic approximation for $\bar{\beta} = 0.01$.

convenient, for the sake of simplicity, to discuss a free energy without a cubic first-harmonic term, *e.g.*, the free energy of the square structure (see eq. (5)). First we notice that there is a new scale of temperature α associated with the quadratic term of the second-harmonic correction. For $\tau > -\alpha$ the quadratic correction increases the free energy and (at $\mu = 0$) the minimum corresponds to $\phi = 0$: only for temperatures smaller than $-\alpha$ does the second harmonic contribute to lower the free energy. It is then natural to introduce the new rescaled variables $\bar{\tau} = \tau/\alpha$, $\bar{\mu} = \mu/(\alpha\lambda)^{1/2}$ and $\{\bar{\psi}, \bar{\phi}\} = (\lambda/\alpha)^{1/2}\{\psi, \phi\}$. This rescaling also shows that the second-harmonic correction becomes important for asymmetries $\mu \gtrsim (\alpha\lambda)^{1/2}$, beyond which the $\psi^2\phi$ coupling term significantly changes the balance in the free energy (for example, in the case of the square free energy a tricritical point appears for $\bar{\mu} = \sqrt{3/4}$ where the transition becomes first-order with a strong component of the second-harmonic parameter). It is then clear that the standard first-harmonic approximation accurately describes the region in the phase diagram where $|\tau| < \alpha$ and $\mu < (\alpha\lambda)^{1/2}$. In practice α is finite even for a second-order phase transition and we need to include higher harmonics in the free energy to describe the regions of the phase diagram where $|\tau| > \alpha$ and $\mu > (\alpha\lambda)^{1/2}$. The same arguments apply to higher harmonics than the second, and our description of the phase-transition, based upon a truncation at the second-harmonic level, will remain accurate for temperatures and asymmetries up to $|\tau| \simeq \gamma$ and $\mu \simeq (\gamma\lambda)^{1/2}$, respectively, where we have defined $\gamma = S(q_s)^{-1} - \tau$. Of course for higher values of q the density of reciprocal lattice points becomes much larger and, depending on the form of $S(q)$, it may become increasingly difficult to choose a cut-off in q-space for the sum in eq. (4). Nonetheless, for many systems we may expect, over a reasonable range of τ and μ, that the second-harmonic approximation yields a significant improvement over the usual treatment.

Finally we point out that although our treatment is based on mean-field theory, the

harmonics corrections should also play a role [13, 21] in more sophisticated theories. For example the Hartree approach [21] is appropriate for weakly first-order transitions (when μ is not too large). Clearly, if the transition is weak enough, then $S(q)$ is almost divergent and second-harmonic corrections to the free energies are small compared to the leading terms. However, in practice the Hartree theory is useful even for moderately first-order transitions [23, 7, 11] in which case the harmonic corrections to the phase diagram may well prove significant.

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Additional Remark. – In principle one may extend these calculations by allowing complex rather than real order parameters in eq. 3 and eq. 5. This allows the description of various new structures that are related to FCC but of lower symmetry (see also ref. 3). In addition to these it would be of interest to include an HCP structure. A treatment of the harmonic corrections that includes these further phases has been developed by M. Olvera and A. M. Mayes (to be published). We are very grateful to Prof. Monica Olvera for a series of very illuminating discussions on the relation between this work and our own.

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