PHYSICAL REVIEW E VOLUME 58, NUMBER 3 SEPTEMBER 1998

Stability of the order-order critical points of Heisenberg and nematic model fluids

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(Received 16 April 1998)

Recently it was found that Heisenberg and nematic model fluids exhibit, for a range of (negative) values of the ratio R of anisotropic to isotropic interaction strengths, a new type of critical point corresponding to the terminus of a first-order phase transition between two orientationally ordered liquids with different densities. In this paper we present a more systematic and detailed study of these order-order critical points (OOCPs). We start by deriving the equations for the OOCPs and solve them numerically, within a mean-field (MF) approximation for the free energies of either model. We then investigate local stability by expanding the free energies in powers of the order parameter, about the lines of OOCPs. In addition, we examine the stability of the OOCPs with respect to the ordered-liquid–ordered-solid transition (global stability), by bifurcation analysis. We conclude that the MF OOCPs are locally and globally stable over a range of $R<0$ which is much broader in the case of the Heisenberg fluid, where the ordering transition is continuous. Here the line of OOCPs ends at a fourth-order critical point on the Curie line, whereas that of the model nematic ends at a critical end point on the nematic-isotropic coexistence curve. Finally, we discuss the relationship between our approach to the stability of critical points and Landau theory. [S1063-651X(98)07309-7]

PACS number(s): 61.20.Gy, 64.60.Cn, 71.10.−w

I. INTRODUCTION

Two of the simplest model fluids with anisotropic interactions are the ferromagnetic Heisenberg fluid (FHF) [1] and the Maier-Saupe liquid crystal (MSLC) [2], characterized, respectively, by the pair potentials [3]

$$\phi_{\rm FHF}(\mathbf{r}_{12},\omega_1,\omega_2)=\begin{cases}+\infty & \text{if } r\leqslant\sigma\\ -I_{\rm FHF}(r_{12})-J_{\rm FHF}(r_{12})P_1[\cos(\omega_1,\omega_2)] & \text{if } r>\sigma\end{cases} \tag{1}$$

and

$$\phi_{\rm MSLC}(\mathbf{r}_{12},\omega_1,\omega_2)=\begin{cases}+\infty & \text{if } r\leqslant\sigma\\ -I_{\rm MSLC}(r_{12})-J_{\rm MSLC}(r_{12})P_2[\cos(\omega_1,\omega_2)] & \text{if } r>\sigma,\end{cases} \tag{2}$$

where $\mathbf{r}_{12}$ is the intermolecular vector of length r_{12}, ω_i is the set of orientational coordinates (Euler angles) of molecule i, σ is the diameter of the (spherical) hard core, $P_k(x)$ is the kth Legendre polynomial, and $J(r_{12})$ and $I(r_{12})$ are the radial parts of, respectively, the anisotropic and the (soft) isotropic interactions.

Both models exhibit orientationally ordered liquid phases: at high enough densities or low enough temperatures, the former is a ferromagnet [1,4–6], and the latter a nematic [2,7]. Extensive mean-field (MF) calculations have shown that the overall topology of their phase diagrams depends sensitively on the ratio R of the integrated strengths of the isotropic and anisotropic interactions, given by

$$R=\frac{\int d\mathbf{r}_{12}J(r_{12})}{\int d\mathbf{r}_{12}I(r_{12})}=\frac{J_{\rm int}}{I_{\rm int}}. \tag{3}$$

In particular, R determines what types of critical points obtain. These findings are summarized in Tables I and II. If $-1.04<R<0$ there is no liquid-vapor (L-V) coexistence, as the anisotropic attractions are insufficient to drive condensation for such strong isotropic repulsions. In the case of the FHF, varying the *ranges* of $I(r_{12})$ and $J(r_{12})$ shifts the crossovers to different values of R [6] and allows a given type of diagram to be generated in different ways [8], but does not otherwise introduce any new physics. Interestingly, the same topologies as the FHF's (for $R>0$) have surfaced in a Monte Carlo and MF probe of a symmetrical binary fluid mixture, where the role of R is played by the relative strength of interactions between unlike and like species. This somewhat unexpected convergence of behaviors was explained, within Landau theory, by realizing that in either model the density is coupled with a ‘‘spinlike’’ internal degree of freedom [9].

The possibility, within both MF [5] and modified MF [6] theories, of an order-order critical point (OOCP) in the FHF or the MSLC characterized by soft *repulsive* isotropic interactions ($I_{\rm int}<0$), is noteworthy. However, this has only been corroborated by a mean spherical approximation study of a purely *anisotropic* FHF ($I_{\rm int}=0$) [10], for which simulation evidence is available but (inconclusively) seems to favor a tricritical point instead [4]. OOCPs where the ordered phases are *nematic* have been predicted to occur in systems of rodlike particles with added attractions [11–17]; it is as yet unclear whether these have been observed experimentally [18–20]. In the one model that has been simulated, namely, hard spherocylinders with attractive square wells, nematic-nematic (N-N) coexistence is preempted by the formation of a smectic-A phase [17]. By contrast, in neither the FHF nor

TABLE I. Topology of the phase diagram of the FHF from MF theory [1,5]. A refined calculation using modified MF theory [6] yields crossovers at different values of R than MF, but does not change the scenario qualitatively. CEP: critical end point; TCP: tricritical point L-V: liquid-vapor, OOCP: order-order critical point.

R	Ordering transition(s)	Critical point
$0<R<0.38$ ([5], Fig. 1)	Changes order at CEP	Isotropic L-V
$0.38<R<0.63$ ([5], Fig. 2)	Changes order at TCP	Isotropic L-V
$R>0.63$; $R<-25.2$ ([5], Fig. 3)	Changes order at TCP	None
$-25.2<R<-1.04$ ([5], Fig. 8)	Continuous above OOCP; one continuous, one first order between OOCP and CEP; first order below CEP	OOCP
$-1.04<R<0$	Always continuous	None

the MSLC is there coupling between orientational and positional degrees of freedom, and for that reason they do not form smectic phases [21]. If real, the OOCP would be the orientational analog of the solid-solid critical points found in Cs, SmS, and Ce-Th mixtures [22–26]; in Monte Carlo studies of model colloids [27,28]; and theoretically [29–44].

In previous work we used molecular theory to calculate the different types of phase diagram for both the FHF [5,6] and the MSLC [7], and discussed the criticality of the former in detail [5]. Here we explicitly locate the OOCPs as a function of R, and investigate their stability, both local and global. This paper is organized as follows. In Sec. II we derive the equations for the OOCP in a general fluid with anisotropic interactions; these are then solved numerically, within the MF approximation, for the two models under consideration. In Sec. III we examine the local stability of the previously computed OOCPs by expanding the free energy densities about them. Then in Sec. IV we calculate the limit of stability of the ordered liquid phases of the FHF and MSLC with respect to the corresponding ordered solids; because neither model exhibits a smectic phase, this allows us approximately to check the global stability of the OOCPs. Finally in Sec. V we summarize our conclusions, and discuss the relationship between our approach to local stability and the more common analysis in terms of Landau theory.

II. CRITICALITY

Let $f \equiv f(\rho,\eta,T)$ be the Helmholtz free energy density (FED) of a fluid characterized by the (uniform) density ρ, the order parameter η, and the temperature T. Then criticality is studied by considering the stability matrix $\mathbf{M}$ [5]:

$$\mathbf{M}=\begin{pmatrix} \left(\dfrac{\partial^2 f}{\partial \rho^2}\right)_\eta & \dfrac{\partial^2 f}{\partial\rho\partial\eta} \\ \dfrac{\partial^2 f}{\partial\rho\partial\eta} & \left(\dfrac{\partial^2 f}{\partial \eta^2}\right)_\rho \end{pmatrix}.$$

The first necessary condition to have a critical point is that the determinant of $\mathbf{M}$ vanish:

$$\det \mathbf{M}=\left(\frac{\partial^2 f}{\partial \rho^2}\right)_\eta \left(\frac{\partial^2 f}{\partial \eta^2}\right)_\rho - \left(\frac{\partial^2 f}{\partial\rho\partial\eta}\right)^2 =0. \tag{4}$$

This is the two-dimensional [in (ρ,η) space] generalization of the requirement that the compressibility diverge at the L-V critical point.

In order to establish a second necessary condition, we need to find the eigenvector (u,v) corresponding to the zero eigenvalue of $\mathbf{M}$. This is

$$(u,v)=\left(1,-\frac{M_{11}}{M_{12}}\right) \quad \text{or} \quad (u,v)=\left(-\frac{M_{12}}{M_{22}},1\right). \tag{5}$$

(u,v) defines a direction in (ρ,η) space that can be parametrized by δ (see Fig. 1). For an isotropic critical point, $(u,v)=(1,0)$ (because all $M_{ij}=0$ except M_{22}); and for a point on the order-disorder line, $(u,v)=(0,1)$ (because all $M_{ij}=0$ except M_{11}). In the present case of an OOCP, none of the elements of $\mathbf{M}$ is zero, and so we have to use one of the general expressions of Eq. (5). This yields the condition that the third derivative of f along the direction (u,v) vanish at the critical point, i.e.,

$$u^3\left(\frac{\partial^3 f}{\partial\rho^3}\right)_\eta + 3u^2 v\,\frac{\partial^3 f}{\partial\rho^2\partial\eta} + 3uv^2\frac{\partial^3 f}{\partial\rho\partial\eta^2} + v^3\left(\frac{\partial^3 f}{\partial\eta^3}\right)_\rho =0. \tag{6}$$

The third and final condition is that in zero field, the FED must not contain any linear dependence on the order parameter:

$$\left(\frac{\partial f}{\partial\eta}\right)_\rho =0. \tag{7}$$

TABLE II. Topology of the phase diagram of the MSLC from MF theory [2,7]. Unlike in the FHF, the ordering transition is always first order. Abbreviations as in Table I.

R	Critical point
$0<R<0.79$ ([7], Fig. 1)	Isotropic L-V
$R>0.79$; $R<-1.64$ ([7], Fig. 3)	None
$-1.64<R<-1.04$ ([7], Fig. 3)	OOCP

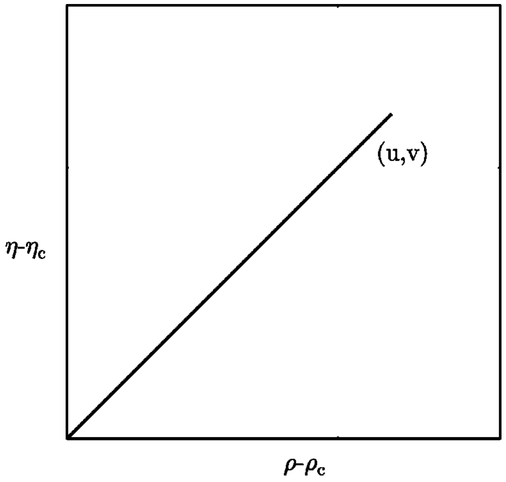

FIG. 1. Schematic representation of the direction (u,v), fixed for each critical point, and along which the free energy is expanded. This direction is parametrized by δ, the order parameter of the transition, which is linearly related to ρ and η_i.

The critical point (ρ_c,η_c,T_c) can now be found by solving Eqs. (4), (6), and (7) simultaneously, for given choices of interaction parameters. We thus require expressions for the FEDs of the FHF and the MSLC. In the spirit of perturbation theory, let us write the intermolecular potential as

$$\phi(\mathbf{r}_{12},\omega_1,\omega_2)=\phi_{\mathrm{ref}}(\mathbf{r}_{12})+\phi_p(\mathbf{r}_{12},\omega_1,\omega_2), \tag{8}$$

where $\phi_{\mathrm{ref}}(\mathbf{r}_{12})$ is the hard-sphere (HS) ''reference'' part, and $\phi_p(\mathbf{r}_{12},\omega_1,\omega_2)$ the longer-ranged ''tail'' of either $\phi_{\mathrm{FHF}}(\mathbf{r}_{12},\omega_1,\omega_2)$ or $\phi_{\mathrm{MSLC}}(\mathbf{r}_{12},\omega_1,\omega_2)$ in Eq. (1) or (2), respectively. The MF Helmholtz free energy is then

$$\begin{aligned}\mathcal{F}[\rho(\mathbf{r},\omega)]=\mathcal{F}_{\mathrm{ref}}[\rho(\mathbf{r},\omega)]+\frac{1}{2}\int d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2\\ \times\rho(\mathbf{r}_1,\omega_1)\phi_p(\mathbf{r}_{12},\omega_1,\omega_2)\rho(\mathbf{r}_2,\omega_2),\end{aligned} \tag{9}$$

where $\rho(\mathbf{r},\omega)$ is the density-orientational profile. The free energy of the reference system, $\mathcal{F}_{\mathrm{ref}}[\rho(\mathbf{r},\omega)]$, consists of ideal-gas and excess contributions, the latter due to the excluded volume interaction:

$$\begin{aligned}\mathcal{F}_{\mathrm{ref}}[\rho(\mathbf{r},\omega)]=\beta^{-1}\int d\mathbf{r}d\omega\rho(\mathbf{r},\omega)\{\ln[\Lambda^3\rho(\mathbf{r},\omega)]-1\}\\ +\mathcal{F}_{\mathrm{HS}}^{\mathrm{exc}}[\rho(\mathbf{r})],\end{aligned} \tag{10}$$

where $\beta=1/k_BT$, Λ is the thermal de Broglie wavelength, $\rho(\mathbf{r})=\int d\omega\rho(\mathbf{r},\omega)$, and the orientational entropy is described in the random-mixing approximation. In a uniform (or weakly nonuniform) fluid, the excess free energy can be treated in a local approximation (but see Sec. IV below):

$$\mathcal{F}_{\mathrm{HS}}^{\mathrm{exc}}[\rho(\mathbf{r})]=\int d\mathbf{r}\rho(\mathbf{r})\Psi(\rho(\mathbf{r})), \tag{11}$$

with $\Psi(\rho)$ an excess HS free energy per particle, to be specified later.

The free energy density of an orientationally ordered, but positionally disordered, phase of density ρ, is now

$$\begin{aligned}f(\rho,\eta)=f_{\mathrm{HS}}(\rho)+\rho\beta^{-1}\langle\ln[4\pi\hat{f}(\omega)]\rangle-\frac{1}{2}I_{\mathrm{int}}\rho^2\\ -\frac{1}{2}J_{\mathrm{int}}\rho^2\eta_i^2,\end{aligned} \tag{12}$$

where $f_{\mathrm{HS}}(\rho)=\rho\beta^{-1}[\ln(\Lambda^3\rho)-1]+\rho\Psi(\rho)$, $\hat{f}(\omega)=\rho(\omega)/\rho$ is the orientational distribution function (ODF), and $\langle A\rangle=\int d\omega A\hat{f}(\omega)$. In Eq. (12), η_i is the orientational order parameter, defined as

$$\eta_i=\int P_i(\cos\theta)\hat{f}(\omega)d\omega. \tag{13}$$

($i=1$ for the FHF and $i=2$ for the MSLC.) Minimizing the FED with respect to the ODF (see, e.g., [2]), we obtain

$$\hat{f}(\omega)=\frac{\exp[\beta J_{\mathrm{int}}\rho\eta_iP_i(\cos\theta)]}{\int\exp[\beta J_{\mathrm{int}}\rho\eta_iP_i(\cos\theta)]d\omega}. \tag{14}$$

Substitution of Eq. (14) into Eq. (12) yields, for the equilibrium FED,

$$f(\rho,\eta_i)=f_{\mathrm{HS}}(\rho)-\frac{1}{2}I_{\mathrm{int}}\rho^2+\frac{1}{2}J_{\mathrm{int}}\rho^2\eta_i^2-\rho\beta^{-1}\alpha(\beta J_{\mathrm{int}}\rho\eta_i), \tag{15}$$

where

$$\alpha_{\mathrm{FHF}}(x)=\ln\left(\frac{\sinh x}{x}\right), \tag{16}$$

$$\alpha_{\mathrm{MSLC}}(x)=\ln\left[\frac{\mathcal{D}\left(\sqrt{\frac{3}{2}x}\right)}{\sqrt{\frac{3}{2}x}}\right], \tag{17}$$

and $\mathcal{D}(x)=\exp(-x^2)\int_0^x\exp(t^2)dt$ is Dawson's integral.

For consistency with previous work [5–7], we take

$$I_{\mathrm{FHF}}(r_{12})=\epsilon_{\mathrm{iso}}\left(\frac{\sigma}{r_{12}}\right)^6, \tag{18}$$

$$J_{\mathrm{FHF}}(r_{12})=\epsilon_{\mathrm{ani}}\frac{e^{-(r_{12}/\sigma-1)}}{r_{12}/\sigma}, \tag{19}$$

$$\beta\Psi_{\mathrm{FHF}}(\rho)=\xi\frac{4-3\xi}{(1-\xi)^2}, \tag{20}$$

$$I_{\mathrm{MSLC}}(r_{12})=\epsilon_{\mathrm{iso}}\left(\frac{\sigma}{r_{12}}\right)^6, \tag{21}$$

$$J_{\mathrm{MSLC}}(r_{12})=\epsilon_{\mathrm{ani}}\left(\frac{\sigma}{r_{12}}\right)^6, \tag{22}$$

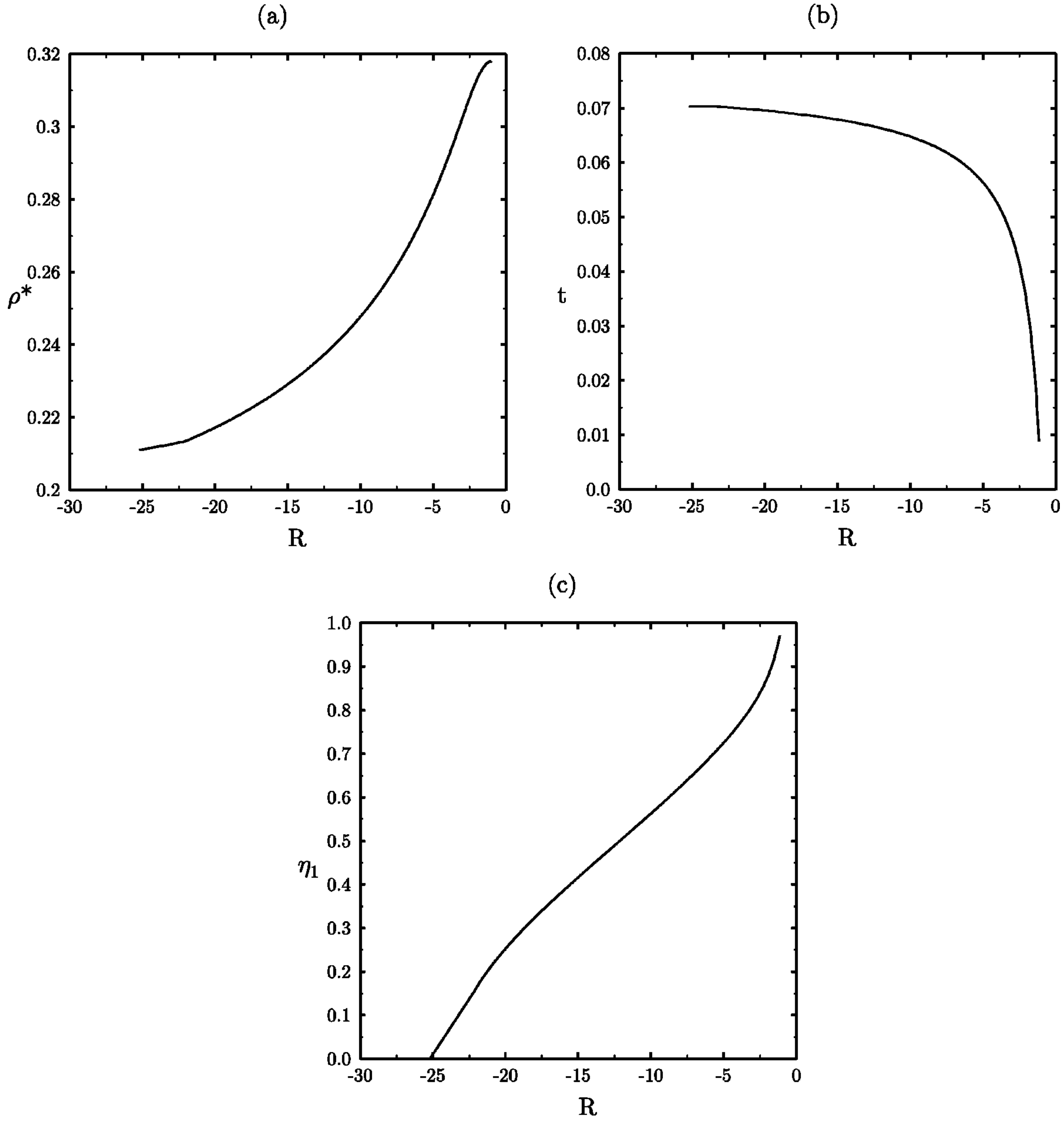

FIG. 2. (a) Reduced density $\rho^*=\rho\sigma^3$; (b) reduced temperature $t=k_BT_c\sigma^3/J_{\mathrm{FHF,int}}$; and (c) order parameter η_1 at the OOCP of the FHF.

$$\beta\Psi_{\mathrm{MSLC}}(\rho)=\rho\left[-\ln(1-\xi)+\frac{6\xi-9\xi^2+3\xi^3}{2(1-\xi)^3}\right]. \quad (23)$$

Equations (20) and (23) are, respectively, the Carnahan-Starling [45] and Percus-Yevick (compressibility) [46,47] approximations to the excess FED of a HS liquid, and $\xi=\pi\rho\sigma^3/6$ is the packing fraction.

In what follows all results are given in terms of the reduced density $\rho^*=\rho\sigma^3$ and reduced temperature $t=k_BT\sigma^3/J_{\mathrm{int}}$. In subscripts, ‘‘$c$’’ will be used as an abbreviation of ‘‘OOCP.’’

Figure 2 shows the density, temperature, and order parameter at the OOCP of the FHF, as functions of R. In an earlier paper [5] we found that the OOCP should transform into a tricritical point on the Curie line (the locus of continuous disorder-order transitions of the FHF model, given by $\beta\rho J_{\mathrm{FHF,int}}=3$), at a fourth-order critical point [48] characterized by $R=R_{\mathrm{4th}}$. This is borne out by Fig. 3, where we plot the quantity $x=\beta_c\rho_cJ_{\mathrm{FHF,int}}$; clearly $x\to 3$ as $R\to R_{\mathrm{4th}}\approx -25.2$.

In the MSLC the corresponding line of continuous disorder-order transitions is $\beta\rho J_{\mathrm{MSLC,int}}=5$, but this is always inside the nematic-isotropic (N-I) coexistence region [7], thence a less rich critical behavior, see Table II. In Fig. 4 we show densities, temperatures, and order parameters at the OOCP and at the N-N-I triple point. In contrast to the FHF, there are now two branches of OOCPs; the lower branch (dotted lines) lies outside the region where N-N coexistence is possible [see Fig. 4(a)] and is therefore unphysical (in addition, we shall see in the next section that it is also locally unstable). The same is true of that part of the upper branch for which $R\lesssim -1.64$. We conclude that the line of OOCPs for the MSLC ends at a critical end point on the N-N coexistence curve. One further difference between the FHF and

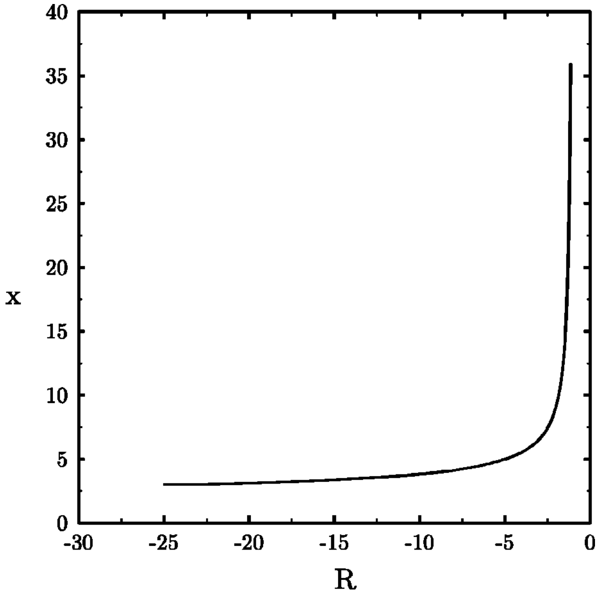

FIG. 3. $x=\beta_c\rho_c J_{\mathrm{FHF,int}}$ vs R for the FHF. x approaches 3 as $R\to-25.2$, meaning that the OOCP is approaching the Curie line, and hence $\eta_c\to 0$.

the MSLC is apparent from comparison of Figs. 3 and 5(a): in the latter, the line of OOCPs does not approach the line of disorder-order transitions, $x=5$. This is illustrated in Fig. 5(b), which plots ρ_c^* vs t_c.

III. LOCAL STABILITY

One of the methods employed in [5] to investigate the existence of OOCPs in the FHF was to perform an expansion of the FED about the Curie line, or the tricritical point, and analyze the signs of the first six coefficients of that expansion [49]. This enabled us to state that for $0.63<R<\infty$ we have a tricritical point, and for $R\approx-25.2$ a fourth-order point. For $0>R\gtrsim-25.2$ the tricritical point becomes unstable and so a new type of criticality must appear. In the preceding section, we explicitly calculated the OOCPs; they correspond to solutions of Eqs. (4), (6), and (7) with $\eta_c\neq 0$ and $\beta_c\rho_c J_{\mathrm{int}}>3$ or 5, and so their stability cannot be studied by examining an expansion about the order-disorder line, on which $\eta_c=0$; one has to generalize this expansion to nonzero η_c. To obtain the original expansion about the Curie points, the Helmholtz FED, Eq. (15), was first Legendre transformed to a new thermodynamic potential with variables η (the order parameter of the transition), μ (the field corresponding to the other density), and T. This new potential, denoted $g_\eta(\eta,\mu,T)$, was then expanded in powers of η, and, because the derivatives of g_η with respect to η were taken at constant μ, the coefficients of the expansion could be written in terms of derivatives of $f(\rho,\eta)$ with respect to both η and ρ. In the present problem, one might expand an appropriate thermodynamic potential g_δ in the order parameter of the OOCP, δ (see Fig. 1). However, for each OOCP (i.e., for each R) the direction (u,v) is fixed in (ρ,η) space. Therefore δ is linearly related to both η and ρ, and one can perform instead an expansion in η or in ρ, using $g_\eta(\eta,\mu,T)$ or $g_\rho(\rho,H,T)$. Here we calculate the expansion of $g_\eta(\eta,\mu,T)$ in η about η_c, but it can be shown that the same results (for coexistence and criticality) follow from an expansion of $g_\rho(\rho,H,T)$ in ρ.

At constant μ and T, we then have [49]

$$g_\eta(\eta,\mu,T)=\sum_{n=0}^{\infty}A_n\tilde{\eta}^n, \tag{24}$$

where $\tilde{\eta}=\eta-\eta_c$, and

$$A_n=\frac{1}{n!}\left(\frac{\partial^n g_\eta}{\partial\eta^n}\right)_{T,\mu}. \tag{25}$$

The coefficients A_n are to be evaluated at the OOCP, (ρ_c,η_c). A_1 is, of course, the applied field, which can be calculated in terms of ρ and η using Eq. (15):

$$A_1=\left(\frac{\partial g_\eta}{\partial\eta}\right)_{T,\mu}=\left(\frac{\partial f}{\partial\eta}\right)_\rho=H(\rho,\eta). \tag{26}$$

The other coefficients can also be written in terms of ρ and η by applying the operator Θ to the field $H(\rho,\eta)$:

$$\Theta=\left(\frac{\partial}{\partial\eta}\right)_{T,\mu}=\left[\left(\frac{\partial}{\partial\eta}\right)_\rho-\frac{\partial^2 f/\partial\rho\partial\eta}{(\partial^2 f/\partial\rho^2)_\eta}\left(\frac{\partial}{\partial\rho}\right)_\eta\right]. \tag{27}$$

In the Appendix we collect the expressions for A_2, A_3, and A_4. Notice that Eq. (4) and the vanishing of A_2, and Eq. (6) and the vanishing of A_3, give rise to equivalent conditions. In the spirit of Landau theory [49], A_2 is now expanded in powers of $T-T_c$ [50]:

$$A_2(T)=A_2(T_c)+\frac{1}{2}\left[\frac{\partial}{\partial T}\left(\frac{\partial^2 f}{\partial\eta^2}\right)_\rho-2Y\frac{\partial}{\partial T}\frac{\partial^2 f}{\partial\rho\partial\eta}+Y^2\frac{\partial}{\partial T}\left(\frac{\partial^2 f}{\partial\rho^2}\right)_\eta\right](T-T_c), \tag{28}$$

with $Y=(\partial^2 f/\partial\rho\partial\eta)/(\partial^2 f/\partial\rho^2)_\eta$. Using the fact that A_2 and A_3 vanish at the critical point, Eq. (24) with Eq. (15) gives, to fourth order,

$$f=A_0(T_c,\rho_c,\eta_c)+a_2(T_c,\rho_c,\eta_c)(T-T_c)\tilde{\eta}^2+A_4(T_c,\rho_c,\eta_c)\tilde{\eta}^4, \tag{29}$$

where

$$a_2(T_c,\rho_c,\eta_c)=\frac{1}{2}\left\{\left[\frac{\partial}{\partial T}\left(\frac{\partial^2 f}{\partial\eta^2}\right)_\rho\right]_{T_c,\rho_c,\eta_c}-2Y\left(\frac{\partial}{\partial T}\frac{\partial^2 f}{\partial\rho\partial\eta}\right)_{T_c,\rho_c,\eta_c}+Y^2\left[\frac{\partial}{\partial T}\left(\frac{\partial^2 f}{\partial\rho^2}\right)_\eta\right]_{T_c,\rho_c,\eta_c}\right\}. \tag{30}$$

Minimizing Eq. (29) with respect to η, we find as usual

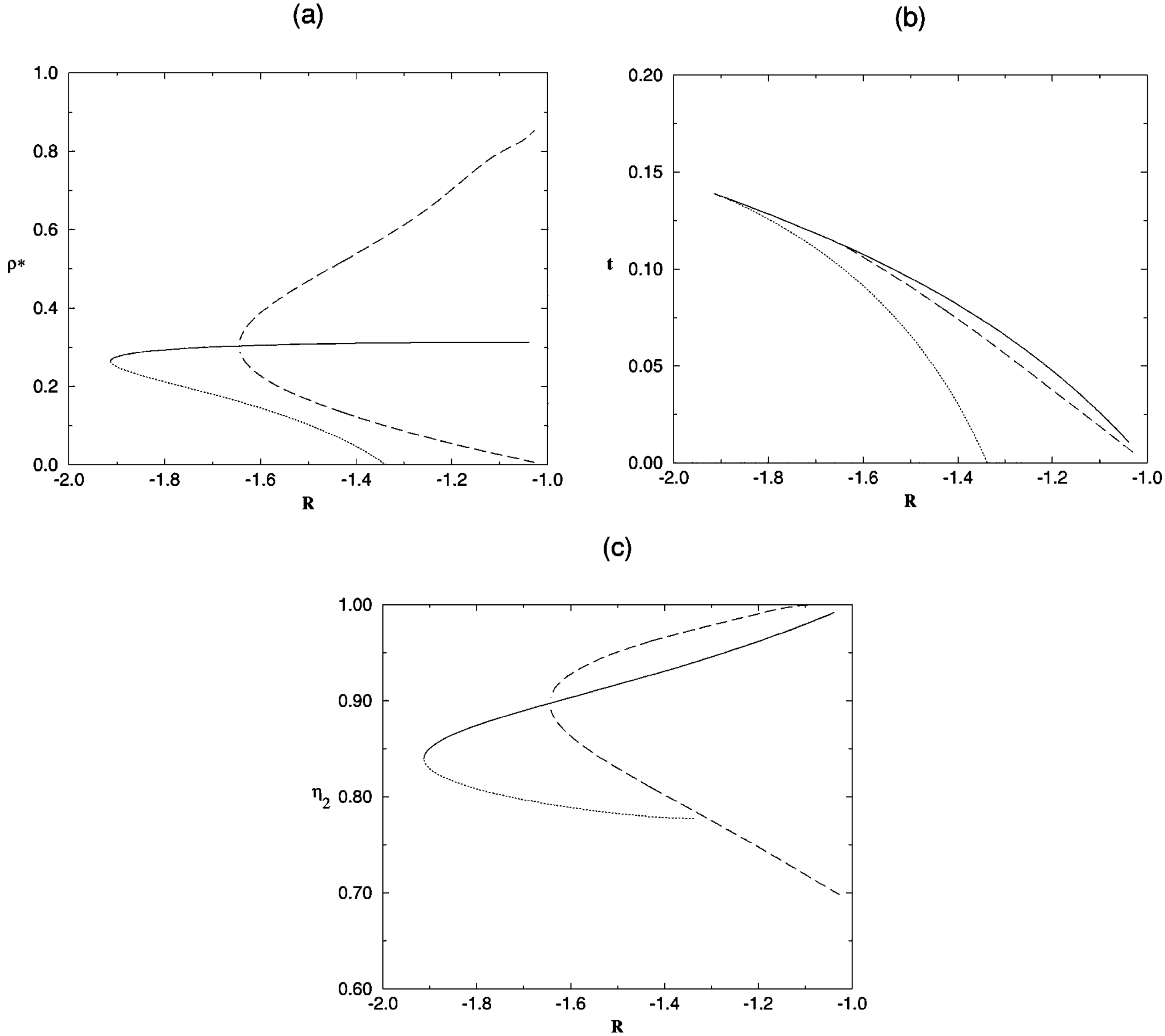

FIG. 4. (a) Reduced density $\rho^*=\rho\sigma^3$; (b) reduced temperature $t=k_BT\sigma^3/J_{\mathrm{MSLC,int}}$; and (c) order parameter η_2 of the MSLC. Solid lines: locally stable branch of OOCPs; dotted lines: locally unstable branch of OOCPs. Dashed lines: same quantities at the *N*-*N*-*I* triple point.

$$\tilde{\eta}=\pm\sqrt{\frac{a_2(T_c,\rho_c,\eta_c)(T_c-T)}{2A_4(T_c,\rho_c,\eta_c)}}. \tag{31}$$

From the linear dependence of (ρ,η) on δ, it is possible to find a relation between η and ρ in the vicinity of the OOCP:

$$\tilde{\rho}=\left(\frac{(\partial^2 f/\partial\eta^2)_\rho}{\partial^2 f/\partial\rho\partial\eta}\right)_{T_c,\rho_c,\eta_c}\tilde{\eta}. \tag{32}$$

Numerical results are presented in Fig. 6. For the FHF, $A_4(T_c,\rho_c,\eta_c)$ is always positive and approaches zero with vanishing slope as $R\rightarrow R_{4\mathrm{th}}\approx-25.2$, corresponding to a locally stable OOCP over the whole range of R for which it exists (see preceding section). For the MSLC, $A_4(T_c,\rho_c,\eta_c)>0$ along the upper branch of OOCPs, which are thus locally stable whenever physical ($R>-1.64$); whereas the lower branch has $A_4(T_c,\rho_c,\eta_c)<0$ and is therefore unstable, as announced in the preceding section. The two branches are connected at $R\approx-1.91$, where the slope of the curve is infinite (however, this point lies in the unphysical region).

IV. STABILITY WITH RESPECT TO THE SOLID PHASE

The analysis of the stability of the OOCP will only be complete with a study of stability relative to the solid phase (global stability), i.e., of whether fluid-solid coexistence preempts coexistence of two ordered fluids for any of the values of R for which the OOCP is locally stable. At first sight, this would not appear to be possible. Indeed, it is short-range repulsive interactions that play the main role in the freezing transition, and freezing of HS does not occur until $\rho^*\approx0.945$ [51], which is far above all OOCP densities of either of our models. Nonetheless, the present OOCPs are obtained for systems with soft *repulsive* isotropic interactions, which

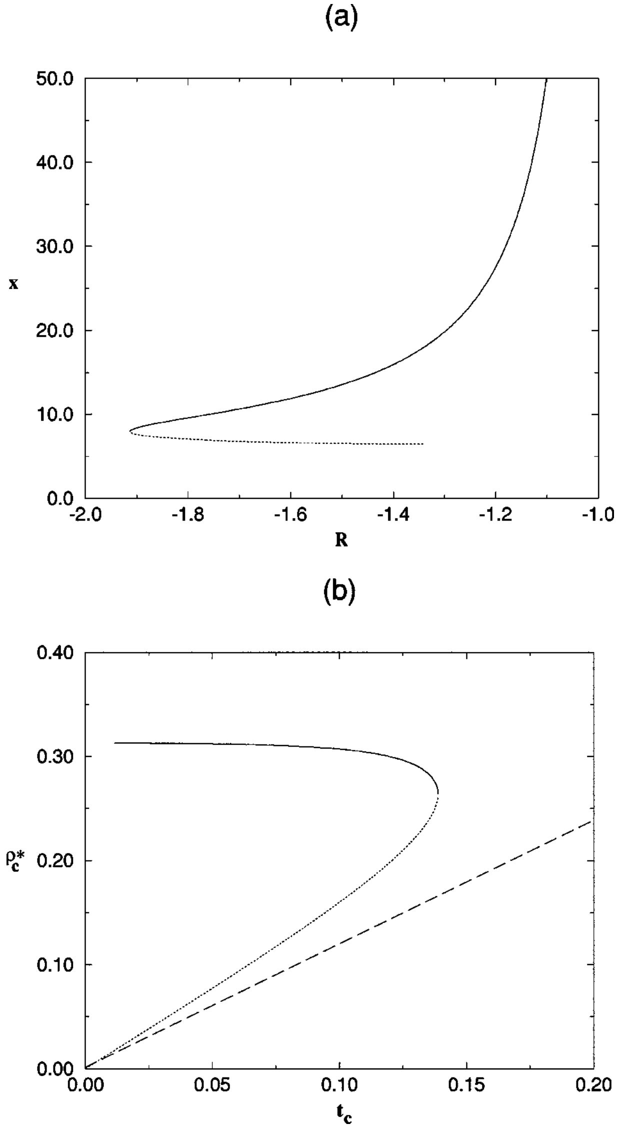

FIG. 5. (a) $x=\beta_c\rho_c J_{\mathrm{MSLC,int}}$ vs R for the MSLC. Solid line: locally stable branch; dotted line: locally unstable branch. In contrast to the FHF (cf. Fig. 3), η_c is always finite. (b) ρ_c^* $(=\rho_c\sigma^3)$ vs t_c $(=k_BT_c\sigma^3/J_{\mathrm{MSLC,int}})$; the straight dashed line is the limit of absolute stability of the isotropic phase with respect to the nematic, $x=5$.

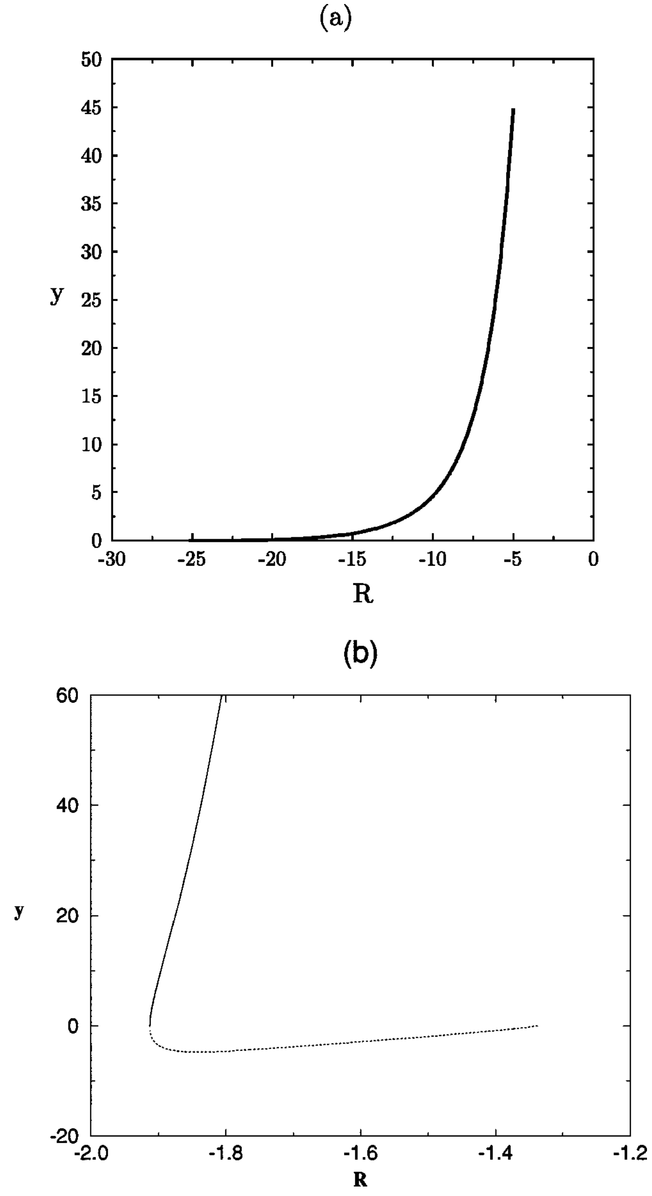

FIG. 6. Reduced fourth-order coefficient $y=\beta_c A_4(T_c,\rho_c,\eta_c)$ of the FED expansion about the OOCP for (a) the FHF and (b) the MSLC; it vanishes on the Curie line. In (b) the dotted line corresponds to the unstable branch of OOCPs.

may drive down the freezing density.

The easiest way to tackle this problem would be to write down the free energy as in Eq. (15), changing only the form of the excess HS part to a solid parametrization. Such a procedure was employed in [1] for the FHF, but for different values of R than the ones we are interested in. A more elaborate way of deriving an equation of state for the solid can be found in [32,33], where the interaction part is treated in different ways in the liquid and solid phases. However, in both approaches the main features of the solid-liquid transition are determined by the parametrizations chosen for the HS (liquid or solid) equation of state. (A recent van der Waals theory of the FHF including solid phases [8] did not extend to $R<0$.) In [52] and [53], density-functional theories of the freezing transition are proposed. Both provide solid equations of state, and thus enable one to calculate coexistence lines. As at present we are simply interested in the stability of a fluid phase with respect to the solid, rather than in characterizing the fluid-solid transition, we will use none of the above theories, but the simpler bifurcation analysis [54,55]. Here one calculates just the limit of stability of one phase (liquid) with respect to another (solid), and not coexistence between phases.

The bifurcation analysis we adopt has been applied to some transitions in liquid crystal models [54,55]. It states that, if $\rho_A(\mathbf{r},\omega)$ is an equilibrium density profile of phase A, $\rho_B(\mathbf{r},\omega)$ an equilibrium density profile of phase B, and $\delta\rho_{AB}(\mathbf{r},\omega)$ the difference between the density profiles of the two phases, then phase A will be stable with respect to phase B when

$$\int d\mathbf{r}_1 d\omega_1 d\mathbf{r}_2 d\omega_2 \, \delta\rho_{AB}(\mathbf{r}_1,\omega_1)\, \delta\rho_{AB}(\mathbf{r}_2,\omega_2)$$

$$\times \left. \frac{\delta^2 \mathcal{F}[\rho(\mathbf{r},\omega)]}{\delta\rho(\mathbf{r}_1,\omega_1)\,\delta\rho(\mathbf{r}_2,\omega_2)} \right|_{\rho(\mathbf{r},\omega)=\rho_A(\mathbf{r},\omega)} \geqslant 0. \tag{33}$$

We are interested in the stability of an ordered liquid [phase A: $\rho_A(\mathbf{r},\omega)=\rho_L \hat{f}_L(\omega)$] with respect to an ordered solid [phase B: $\rho_B(\mathbf{r},\omega)=\rho_S(\mathbf{r})\hat{f}_S(\omega)$]. In Sec. II we used the simplest, local, approximation for the excess free energy of the HS fluid, Eq. (11). This is inappropriate when the density is strongly inhomogeneous (and can reach very large values, where conventional bulk equations of state break down), as is the case in a solid. We therefore resort to the simplest *nonlocal* scheme, the smoothed-density approximation (SDA) of Tarazona [52] for HSs:

$$\mathcal{F}^{\mathrm{exc}}_{\mathrm{HS}}[\rho(\mathbf{r})]=\int d\mathbf{r}\rho(\mathbf{r})\Psi(\overline{\rho}(\mathbf{r})). \tag{34}$$

Here $\overline{\rho}(\mathbf{r})$ is a functional of the density and has the form

$$\overline{\rho}(\mathbf{r})=\int d\mathbf{r}'\,w(|\mathbf{r}-\mathbf{r}'|)\rho(\mathbf{r}'), \tag{35}$$

where the weighting function $w(|\mathbf{r}-\mathbf{r}'|)$ is the quotient between the Mayer function of two HSs and the second virial coefficient of the HS fluid:

$$w(r)=\begin{cases} \dfrac{3}{4\pi\sigma^3}, & r<\sigma \\ 0, & r\geqslant\sigma, \end{cases} \tag{36}$$

which corresponds to "smearing" any peaks in $\rho(\mathbf{r})$ over the excluded volume of a pair of HSs. We shall retain the same expressions for $\Psi(\rho)$, Eqs. (20) and (23).

By analogy with [56], $\delta\rho_{LS}(\mathbf{r},\omega)$ are expanded as products of Fourier and spherical harmonics series:

$$\delta\rho_{LS}(\mathbf{r},\omega)=\rho_L\hat{f}_L(\omega)\sum_{\mathbf{q}}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\mu_{\mathbf{q}lm} \times\exp(-i\mathbf{q}\cdot\mathbf{r})Y_{lm}(\omega), \tag{37}$$

where $\mathbf{q}$ is a reciprocal lattice vector of the Bravais lattice characterizing the solid phase, and $Y_{lm}(\omega)$ are spherical harmonics describing the difference between the orientational structures of the two phases (only even l are allowed in the case of a MSLC). Furthermore, we expand the ODF of the liquid in Legendre polynomials:

$$\hat{f}_L(\omega)=\sum_{\lambda=0}^{\infty}\frac{2\lambda+1}{4\pi}\,\eta_\lambda P_\lambda(\cos\theta). \tag{38}$$

[As in Eq. (37), for the MSLC only even λ are allowed.]

Inserting Eq. (37) into Eq. (33) and performing the second functional derivative of $\mathcal{F}[\rho(\mathbf{r},\omega)]$, given by Eq. (9) with Eqs. (10) and (34), we find, after straightforward but tedious algebra, that for each wave vector $\mathbf{q}$ the ordered liquid will be stable relative to an ordered solid when the following quadratic form in $\mu_{\mathbf{q}lm}$ is positive definite:

$$\sum_{l_1,l_2}\sum_{m_1}\mu_{\mathbf{q}l_1m_1}\mu^{*}_{\mathbf{q}l_2m_1}\Upsilon^{m_1}_{l_1l_2}(\rho,q)\geqslant 0, \tag{39}$$

where

$$\begin{aligned}\Upsilon^{m_1}_{l_1l_2}(\rho,q)={}&\frac{\beta^{-1}\rho}{4\pi}[(2l_1+1)(2l_2+1)]^{1/2}(-1)^{m_1}\\ &\times\sum_{\lambda=0}^{+\infty}C(l_1l_2\lambda;000)C(l_1l_2\lambda;m_1\underline{m}_1 0)\,\eta_\lambda\\ &+\frac{\rho^2}{4\pi}[(2l_1+1)(2l_2+1)]^{1/2}[\Xi(\rho,q)\\ &-I(q)]\,\eta_{l_1}\eta_{l_2}\delta_{m_1 0}\\ &-\frac{\rho^2}{4\pi}J(q)(-1)^{l_1+l_2}[(2l_1+1)(2l_2+1)]^{1/2}\\ &\times\sum_{\lambda_1,\lambda_2=0}^{+\infty}(-1)^{\lambda_1+\lambda_2}C(il_1\lambda_1;000)\\ &\times C(il_1\lambda_1;m_1\underline{m}_1 0)C(il_2\lambda_2;000)\\ &\times C(il_2\lambda_2;m_1\underline{m}_1 0)\,\eta_{\lambda_1}\eta_{\lambda_2},\end{aligned} \tag{40}$$

where $\underline{m}_1=-m_1$, $C(j_1j_2j;n_1n_2n)$ are Clebsch-Gordan (CG) coefficients in the notation of [57] and, as before, $i=1$ for the FHF and $i=2$ for the MSLC (in the latter case, summations are over even l_k or λ_k only). $I(q)$ and $J(q)$ are the Fourier transforms of $I(r)$ and $J(r)$:

$$\begin{aligned}I_{\mathrm{FHF}}(q)&=\int d\mathbf{r}\,\exp(-i\mathbf{q}\cdot\mathbf{r})I_{\mathrm{FHF}}(r)\\ &=3J_{\mathrm{FHF,int}}(q\sigma)^3\int_{q\sigma}^{\infty}\frac{\sin y}{y^5}dy,\end{aligned} \tag{41}$$

$$\begin{aligned}J_{\mathrm{FHF}}(q)&=\int d\mathbf{r}\,\exp(-i\mathbf{q}\cdot\mathbf{r})J_{\mathrm{FHF}}(r)\\ &=\frac{J_{\mathrm{FHF,int}}}{2q\sigma}\,\frac{\sin(q\sigma)+q\sigma\,\cos(q\sigma)}{1+(q\sigma)^2},\end{aligned} \tag{42}$$

$$\begin{aligned}I_{\mathrm{MSLC}}(q)&=\int d\mathbf{r}\,\exp(-i\mathbf{q}\cdot\mathbf{r})I_{\mathrm{MSLC}}(r)\\ &=3I_{\mathrm{MSLC,int}}(q\sigma)^3\int_{q\sigma}^{\infty}\frac{\sin y}{y^5}dy,\end{aligned} \tag{43}$$

$$\begin{aligned}J_{\mathrm{MSLC}}(q)&=\int d\mathbf{r}\,\exp(-i\mathbf{q}\cdot\mathbf{r})J_{\mathrm{MSLC}}(r)\\ &=3J_{\mathrm{MSLC,int}}(q\sigma)^3\int_{q\sigma}^{\infty}\frac{\sin y}{y^5}dy,\end{aligned} \tag{44}$$

with $I_{\mathrm{int}}=4\pi\epsilon_{\mathrm{iso}}\sigma^3/3$, $J_{\mathrm{int}}=4\pi\epsilon_{\mathrm{ani}}\sigma^3/3$. In Eq. (40), $\Xi(\rho,q)$ is the Fourier transform of the second functional derivative of Eq. (34):

$$\Xi(\rho,q)=2\Psi'(\rho)w(q)+\rho\Psi''(\rho)w^2(q), \tag{45}$$

where $w(q)$ is the Fourier transform of the weighting function, Eq. (36):

$$w(q)=\frac{3}{(q\sigma)^3}[\sin(q\sigma)-(q\sigma)\cos(q\sigma)]. \tag{46}$$

The sums in Eq. (40) need to be truncated for practical purposes. A natural assumption is to retain in the expansion of $\delta\rho_{LS}(\mathbf{r},\omega)$ the lowest-order terms with the rotational symmetry of the order parameters. This amounts to the restrictions $l_1,l_2=0,1$ (FHF) or $l_1,l_2=0,2$ (MSLC). It then follows from the properties of CG coefficients that the sums over λ_k terminate at 2 (FHF) or 4 (MSLC).

The limit of stability of the ordered liquid relative to a perturbation with the symmetry of an ordered solid with wave vector $\mathbf{q}$ is attained when the determinant of $\mathbf{\Upsilon}$ in Eq. (39) changes sign. Noting that $\Upsilon_{l_1l_2}^{m_1}=\Sigma_{m_2}\Upsilon_{l_1l_2}^{m_1m_2}\delta_{m_1m_2}$, $\mathbf{\Upsilon}$ can be treated as a rank 2 tensor with indices (l_1,m_1) and (l_2,m_2), such that $\Upsilon_{l_1l_2}^{m_1m_2}\delta_{m_1m_2}=0$ unless $m_1=m_2$. After lengthy computations, the requirement that det $\mathbf{\Upsilon}$ change sign translates into

$$\Upsilon_{00}^{0}\Upsilon_{11}^{0}=\Upsilon_{10}^{0}\Upsilon_{01}^{0}\quad(\text{FHF}), \tag{47}$$

$$\Upsilon_{00}^{0}\Upsilon_{22}^{0}=\Upsilon_{20}^{0}\Upsilon_{02}^{0}\quad(\text{MSLC}), \tag{48}$$

where we have used the fact that, by symmetry, $\Upsilon_{ii}^{i}=\Upsilon_{ii}^{-i}$ ($i=1$ or 2 for the FHF or MSLC, respectively). Equation (40) then yields, for the FHF,

$$\Upsilon_{00}^{0}=\frac{\beta^{-1}\rho}{4\pi}+\frac{\rho^2}{4\pi}[\Xi_{\text{FHF}}(\rho,q)-I_{\text{FHF}}(q)]-\frac{\rho^2}{4\pi}J_{\text{FHF}}(q)\,\eta_1^2, \tag{49}$$

$$\Upsilon_{11}^{0}=\frac{\beta^{-1}\rho}{4\pi}(1+2\eta_2)+\frac{3\rho^2}{4\pi}[\Xi_{\text{FHF}}(\rho,q)-I_{\text{FHF}}(q)]\,\eta_1^2-\frac{\rho^2}{4\pi}J_{\text{FHF}}(q)\left(\frac{1}{3}+\frac{4}{3}\eta_2+\frac{4}{3}\eta_2^2\right), \tag{50}$$

$$\Upsilon_{10}^{0}=\Upsilon_{01}^{0}=\frac{\sqrt{3}\beta^{-1}\rho}{4\pi}\eta_1+\frac{\sqrt{3}\rho^2}{4\pi}[\Xi_{\text{FHF}}(\rho,q)-I_{\text{FHF}}(q)]\,\eta_1-\frac{\sqrt{3}\rho^2}{4\pi}J_{\text{FHF}}(q)\left(\frac{1}{3}\eta_1+\frac{2}{3}\eta_1\eta_2\right), \tag{51}$$

and, for the MSLC,

$$\Upsilon_{00}^{0}=\frac{\beta^{-1}\rho}{4\pi}+\frac{\rho^2}{4\pi}[\Xi_{\text{MSLC}}(\rho,q)-I_{\text{MSLC}}(q)]-\frac{\rho^2}{4\pi}J_{\text{MSLC}}(q)\,\eta_2^2, \tag{52}$$

$$\Upsilon_{22}^{0}=\frac{\beta^{-1}\rho}{4\pi}\left(1+\frac{10}{7}\eta_2+\frac{18}{7}\eta_4\right)+\frac{5\rho^2}{4\pi}[\Xi_{\text{MSLC}}(\rho,q)-I_{\text{MSLC}}(q)]\,\eta_2^2-\frac{\rho^2}{4\pi}J_{\text{MSLC}}(q)\left(\frac{1}{5}+\frac{4}{7}\eta_2+\frac{36}{35}\eta_4+\frac{20}{49}\eta_2^2+\frac{72}{49}\eta_2\eta_4+\frac{324}{245}\eta_4^2\right), \tag{53}$$

$$\Upsilon_{20}^{0}=\Upsilon_{02}^{0}=\frac{\sqrt{5}\beta^{-1}\rho}{4\pi}\eta_2+\frac{\sqrt{5}\rho^2}{4\pi}[\Xi_{\text{MSLC}}(\rho,q)-I_{\text{MSLC}}(q)]\,\eta_2-\frac{\sqrt{5}\rho^2}{4\pi}J_{\text{MSLC}}(q)\times\left(\frac{1}{5}\eta_2+\frac{2}{7}\eta_2^2+\frac{18}{35}\eta_2\eta_4\right). \tag{54}$$

For fixed T and R, Eqs. (47) and (48) define implicit relations between ρ and q. The limit of stability (i.e., the density above which the ordered liquid becomes unstable) is, within bifurcation theory, the minimum of the curve $\rho=\rho(q)$. Calculation of this minimum using Eq. (47) or (48) generates two conditions that must be solved, together with Eq. (47) or (48), to find the modulus of the wave vector $\mathbf{q_m}$ that destroys the stability of the ordered liquid phase at the lowest density, at a temperature T and for the model characterized by R. Recall that with this theory we merely calculate the limit of stability of the liquid with respect to a solid of the same density (the undercooling branch of the liquid-solid spinodal), and not a coexistence curve: the coexistence density of the ordered liquid with the ordered solid will be a little lower. Furthermore, $\mathbf{\Upsilon}$ depends on $q_m=|\mathbf{q_m}|$ only; this is a consequence of the decoupling of orientational and positional degrees of freedom in the present models (see Sec. I). $q_m=|\mathbf{q_m}|$ gives the lattice constant of the metastable solid that bifurcates from the liquid, but the full symmetry of that solid lattice can only be determined by going to second order in perturbation theory (which is beyond the scope of this paper) [58]. Finally, if $\rho(q)$ should exhibit several minima, the physically relevant one will be at $q_m\sim 2\pi/\sigma$, corresponding to the main peak in the structure factor [58].

Results are plotted in Fig. 7. The dashed lines represent the critical densities ρ_c^* and temperatures t_c for $-25.2<R<-1.04$ (FHF) and $-1.64<R<-1.04$ (MSLC); these have been calculated in Sec. II above. The solid lines are the stability limits ρ_{stab}^* for the same values of R and T. At high temperatures (which correspond to large $|R|$), the OOCPs are stable relative to the solid phases, since $\rho_c^*\ll\rho_{\text{stab}}^*$: the former is typically $\rho_c^*\simeq 0.3$ and the latter $\rho_{\text{stab}}^*\simeq 0.8$ (FHF) or $\rho_{\text{stab}}^*\simeq 0.65$ (MSLC). For smaller $|R|$ (and, correspondingly, lower temperatures), ρ_{stab}^* of the FHF decreases abruptly (around $R\simeq -2.5$); no such trend is evident in the case of the MSLC. When $R=-1.35$ (FHF) or $R=-1.24$ (MSLC), we start to have $\rho_{\text{stab}}^*<\rho_c^*$ (FHF) or $\rho_{\text{stab}}^*<\rho_{\text{tri}}^*$ (MSLC) (where ρ_{tri}^* is the density of the denser of the two N phases at the N-N-I triple point), meaning that at these R's the OOCPs become unstable relative to the solid phases, even if they are stable relative to the other fluid phases up to $R=-1.04$. This signals a crossover from liquid-solid to vapor-solid coexistence at low temperatures.

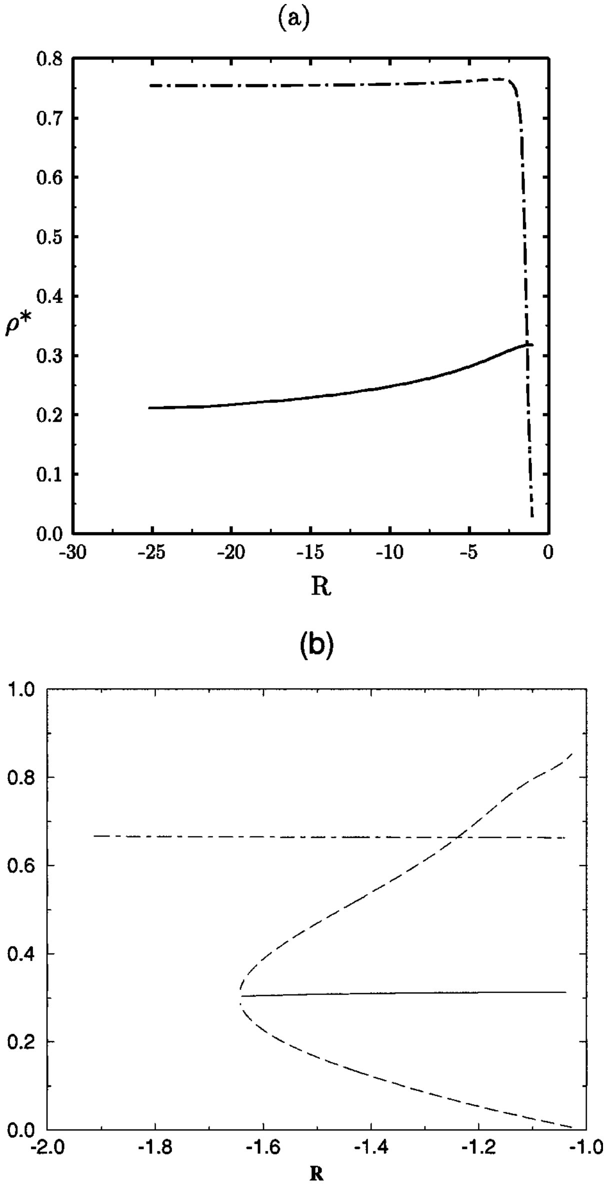

FIG. 7. Reduced densities $\rho^*=\rho\sigma^3$ at the OOCP (solid line) and at the limit of stability of the ordered liquid phase relative to solid fluctuations (dash-dotted line), for (a) the FHF and (b) the MSLC. In (b) the dashed lines are the densities of the two coexisting nematic phases at the *N-N-I* triple point, and only the physically meaningful OOCPs are shown, cf. Fig. 4(a).

V. CONCLUSIONS

We have systematically calculated, and investigated the stability of, OOCPs found previously in molecular field theories of model ferroelectric and nematic fluids. Furthermore, it has been established that the OOCPs are both locally and globally stable over most of the range of temperature and potential parameters for which they exist and are physically meaningful.

The local stability analysis of Sec. III was based on a series expansion of the *equilibrium* microscopic free energy, Eq. (15), about the line of OOCPs and inspection of the fourth-order coefficient. This is standard procedure when the system under study is described by a Landau free energy. In the present case, however, the expression we use, Eq. (29), is *not* a Landau expansion. Still, it is appropriate for our purpose; we next discuss why [59]. Let us consider the simpler case of a MSLC at the *I-N* transition. Katriel *et al.* [60] have presented an example of two expansions of the free energy in the framework of MS theory. The first expression is just the formal (Taylor) expansion of the MF free energy (in zero external field):

$$F=\frac{J_{\mathrm{MSLC,int}}}{2T}(T-T^*)\rho\eta_2^2-\frac{J^3_{\mathrm{MSLC,int}}}{105(k_BT)^2}\rho^3\eta_2^3+\cdots, \tag{55}$$

where $k_BT^*=\rho J_{\mathrm{MSLC,int}}/5$. The second expression is derived in a formally correct way as they describe:

$$F=\frac{5}{2}k_B(T-T^*)\eta_2^2-\frac{25}{21}k_BT\eta_2^3+\cdots. \tag{56}$$

Note that the coefficients in Eqs. (55) and (56) are quite different, but that difference is reduced as $T\rightarrow T^*$ (e.g., at $T=T^*$ the third-order terms are identical). Thus one expects reasonable agreement close to T^*. Let us illustrate this with a simple example: calculate the unstable solution $\eta_2\ll 1$ at $T\gtrsim T^*$. In this case one can neglect higher-order terms and obtain, from the expansion of the MF FED:

$$\eta_2\approx\frac{7}{5}\frac{T-T^*}{T}\left(\frac{T}{T^*}\right)^2, \tag{57}$$

or, from the correct Landau free energy:

$$\eta_2\approx\frac{7}{5}\frac{T-T^*}{T}. \tag{58}$$

These results are formally different, but in fact the same. Indeed, the equations have been obtained by truncating the series after the third-order term. By so doing we restricted ourselves to the leading term in the expansion of η_2 in powers of $(T-T^*)/T^*$, i.e., $\eta_2\sim(T-T^*)/T^*$. However, Eq. (58) and Eq. (57) differ by higher-order terms only, and are therefore equivalent.

Yet it is possible to choose another quantity which will be quantitatively different if calculated by either route: for example, the susceptibility of the isotropic phase. From the Landau expansion we obtain

$$\chi=\frac{1}{5k_B(T-T^*)}, \tag{59}$$

and from the MF free energy expansion:

$$\chi=\frac{1}{5k_B(T-T^*)}\frac{T}{T^*}. \tag{60}$$

Now we are no longer restricted to $T\sim T^*$: the above expressions are *exact*, since no truncation is involved in their derivation. If we take, e.g., $T=1.5T^*$, we can make the difference between them appreciably large.

It is easy to decide which expression is correct. Let us find the susceptibility using the same MF theory: the order parameter in the external field H satisfies

$$\eta_2=\frac{\int P_2(\cos\,\theta)\exp[\beta J_{\mathrm{MSLC,int}}\rho\,\eta_2P_2(\cos\,\theta)+\beta HP_2(\cos\,\theta)]d\omega}{\int\,\exp[\beta J_{\mathrm{MSLC,int}}\rho\,\eta_2P_2(\cos\,\theta)+\beta HP_2(\cos\,\theta)]d\omega}. \tag{61}$$

The susceptibility of the isotropic phase, $\chi=\partial\eta_2/\partial H$, is, from Eq. (61),

$$\chi=\frac{\beta[\langle P_2^2(\cos\,\theta)\rangle_0-\langle P_2(\cos\theta)\rangle_0^2]}{1-\beta\rho J_{\mathrm{MSLC,int}}[\langle P_2^2(\cos\theta)\rangle_0-\langle P_2(\cos\theta)\rangle_0^2]}, \tag{62}$$

where the averages are to be performed at zero field, i.e., $\langle P_2^2(\cos\,\theta)\rangle_0=\int P_2^2(\cos\,\theta)\hat{f}(\omega)d\omega$ with the ODF given by Eq. (14) for $i=2$. From Eq. (62) one recovers Eq. (59) when $n_2\rightarrow 0$, which is the result obtained from the correct Landau free energy expansion.

The reason for the discrepancy is now clear. The susceptibility of the isotropic phase is calculated from an expression taken at zero field. However, that expression itself is derived by employing a free energy functional which depends upon the field. It is obvious that the same result cannot be obtained from another free energy expression valid only at zero field.

We conclude that in zero external field one can use either the correct Landau free energy or the Taylor expansion of the MF expression. However, the latter cannot be called ‘‘Landau free energy’’ because it is not a true Helmholz free energy with the order parameter as an independent variable: it is simply an approximation for the MF free energy at a particular value of the external field. For a different value of the field the corresponding expansion will also be different and has to be derived anew. By contrast, the true Landau expansion is more general (because it is a correct thermodynamic potential) and can be used for *any* value of the external field.

ACKNOWLEDGMENTS

We are grateful to M. A. Osipov and B. M. Mulder for enlightening discussions, to T. J. Sluckin for correspondence, and to T. G. Sokolovska for communicating Ref. [10] prior to publication. J.M.T. acknowledges the financial support of the Portuguese Government in the form of Grant No. PRAXIS XXI/BD/2818/94. M.M.T.G. was partially funded through Portuguese Government contract no. PRAXIS XXI/2/2.1/FIS/181/94. P.I.C.T. acknowledges support from the Engineering and Physical Sciences Research Council (U.K.).

APPENDIX: COEFFICIENTS OF THE LANDAU EXPANSION

The first four coefficients in the expansion of the FED about the OOCP (Sec. II) are

$$A_2=\frac{1}{2}\left[\left(\frac{\partial^2 f}{\partial\eta^2}\right)_\rho-\frac{(\partial^2 f/\partial\rho\partial\eta)^2}{(\partial^2 f/\partial\rho^2)_\eta}\right], \tag{A1}$$

$$A_3=\frac{1}{6}\left[\left(\frac{\partial^3 f}{\partial\eta^3}\right)_\rho-3Y\frac{\partial^3 f}{\partial\rho\partial\eta^2}+3Y^2\frac{\partial^3 f}{\partial\rho^2\partial\eta}-Y^3\left(\frac{\partial^3 f}{\partial\rho^3}\right)_\eta\right], \tag{A2}$$

$$\begin{aligned}A_4=\frac{1}{4!}\Bigg\{&\left(\frac{\partial^4 f}{\partial\eta^4}\right)_\rho-3\frac{(\partial^3 f/\partial\rho\partial\eta^2)^2}{(\partial^2 f/\partial\rho^2)_\eta}\\&+Y\left(-4\frac{\partial^4 f}{\partial\rho\partial\eta^3}+12\frac{(\partial^3 f/\partial\rho\partial\eta^2)(\partial^3 f/\partial\rho^2\partial\eta)}{(\partial^2 f/\partial\rho^2)_\eta}\right)\\&+Y^2\Bigg(6\frac{\partial^4 f}{\partial\rho^2\partial\eta^2}-12\frac{(\partial^3 f/\partial\rho^2\partial\eta)^2}{(\partial^2 f/\partial\rho^2)_\eta}\\&-6\frac{(\partial^3 f/\partial\rho\partial\eta^2)(\partial^3 f/\partial\rho^3)_\eta}{(\partial^2 f/\partial\rho^2)_\eta}\Bigg)\\&+Y^3\left(-4\frac{\partial^4 f}{\partial\rho^3\partial\eta}+12\frac{(\partial^3 f/\partial\rho^2\partial\eta)(\partial^3 f/\partial\rho^3)_\eta}{(\partial^2 f/\partial\rho^2)_\eta}\right)\\&+Y^4\left[\left(\frac{\partial^4 f}{\partial\rho^4}\right)_\eta-3\frac{[(\partial^3 f/\partial\rho^3)_\eta]^2}{(\partial^2 f/\partial\rho^2)_\eta}\right]\Bigg\},\end{aligned} \tag{A3}$$

where $Y=(\partial^2 f/\partial\rho\partial\eta)/(\partial^2 f/\partial\rho^2)_\eta$ as before. We have also calculated A_6 with the aid of MAPLE V but do not present it here, as it is given by a rather lengthy formula.

[1] P. C. Hemmer and D. Imbro, Phys. Rev. A **16**, 380 (1977).
[2] M. M. Telo da Gama, Mol. Phys. **52**, 585 (1984).
[3] Although the intermolecular interactions considered in this paper are invariant under rotations in both position and spin spaces, we call them ‘‘anisotropic’’ for consistency with previous work and with the liquid crystal literature.
[4] E. Lomba, J. J. Weis, N. G. Almarza, F. Bresme, and G. Stell, Phys. Rev. E **49**, 5169 (1994).
[5] J. M. Tavares, M. M. Telo da Gama, P. I. C. Teixeira, J. J. Weis, and M. J. P. Nijmeijer, Phys. Rev. E **52**, 1915 (1995).
[6] J. J. Weis, M. J. P. Nijmeijer, J. M. Tavares, and M. M. Telo da Gama, Phys. Rev. E **55**, 436 (1997).
[7] P. I. C. Teixeira and M. M. Telo da Gama, Mol. Phys. **86**, 1537 (1995).
[8] A. Oukouiss and M. Baus, Phys. Rev. E **55**, 7242 (1997). Following [1] these authors also treat the solid phase, which was not considered in [4–6].
[9] N. B. Wilding, F. Schmid, and P. Nielaba, Phys. Rev. E **58**, 2201 (1998).
[10] T. G. Sokolovska, Physica A **253**, 459 (1998).

[11] P. J. Flory, Proc. R. Soc. London, Ser. A **234**, 73 (1956).
[12] M. Warner and P. J. Flory, J. Chem. Phys. **73**, 6327 (1980).
[13] H. N. W. Lekkerkerker and A. Stroobants, Nuovo Cimento D **16**, 949 (1994).
[14] A. Yu. Grosberg and A. R. Khokhlov, Adv. Polym. Sci. **41**, 53 (1981).
[15] A. R. Khokhlov and A. N. Semenov, J. Stat. Phys. **38**, 161 (1985).
[16] P. I. C. Teixeira, Mol. Phys. **92**, 167 (1997).
[17] P. G. Bolhuis, A. Stroobants, D. Frenkel, and H. N. W. Lekkerkerker, J. Chem. Phys. **107**, 1551 (1997). This work leaves open the possibility of N-N equilibrium in a fluid of infinitely long, hard spherocylinders interacting via a very long-ranged attraction.
[18] C. Casagrande, M. Veyssie, and H. Finkelmann, J. Phys. (France) Lett. **43**, L-671 (1982).
[19] G. Noumesis, C. W. Garland, and R. Shashidar, Phys. Rev. A **43**, 1849 (1991).
[20] H. N. W. Lekkerkerker, P. Buining, J. Buitenhuis, G. J. Vroege, and A. Stroobants, in *Observation, Prediction and Simulation of Phase Transitions in Complex Fluids*, edited by M. Baus, L. F. Rull, and J.-P. Ryckaert (Kluwer, Dordrecht, 1995), pp. 53–112.
[21] J. H. Thurtell, M. M. Telo da Gama, and K. E. Gubbins, Mol. Phys. **54**, 321 (1985).
[22] R. I. Beecroft and C. A. Swenson, J. Phys. Chem. Solids **15**, 234 (1960).
[23] B. L. Davis and L. H. Adams, J. Phys. Chem. Solids **25**, 379 (1964).
[24] A. Jayaraman, Phys. Rev. **137**, A179 (1965).
[25] A. Jayaraman, P. Dernier, and L. D. Longinotti, Phys. Rev. B **11**, 2783 (1975).
[26] J. M. Lawrence, M. C. Croft, and R. D. Parks, Phys. Rev. Lett. **35**, 289 (1975).
[27] P. Bolhuis and D. Frenkel, Phys. Rev. Lett. **72**, 2211 (1994).
[28] P. Bolhuis, M. Hagen, and D. Frenkel, Phys. Rev. E **50**, 4880 (1994).
[29] G. Stell and P. C. Hemmer, J. Chem. Phys. **56**, 4274 (1972).
[30] J. M. Kincaid, G. Stell, and E. Goldmark, J. Chem. Phys. **65**, 2172 (1976).
[31] J. M. Kincaid and G. Stell, J. Chem. Phys. **67**, 420 (1977).
[32] C. F. Tejero, A. Daanoun, H. N. W. Lekkerkerker, and M. Baus, Phys. Rev. Lett. **73**, 752 (1994).
[33] A. Daanoun, C. F. Tejero, and M. Baus, Phys. Rev. E **50**, 2913 (1994).
[34] C. N. Likos, Z. T. Nemeth, and H. Löwen, J. Phys.: Condens. Matter **6**, 10 965 (1994).
[35] C. F. Tejero, A. Daanoun, H. N. W. Lekkerkerker, and M. Baus, Phys. Rev. E **51**, 558 (1995).
[36] Z. T. Nemeth and C. N. Likos, J. Phys.: Condens. Matter **7**, L537 (1995).
[37] C. N. Likos and G. Senatore, J. Phys.: Condens. Matter **7**, 6797 (1995).
[38] C. Rascon, G. Navascués, and L. Mederos, Phys. Rev. B **51**, 14 899 (1995).
[39] C. Rascon, L. Mederos, and G. Navascués, J. Chem. Phys. **103**, 9795 (1995).
[40] T. Coussaert and M. Baus, Phys. Rev. E **52**, 862 (1995).
[41] M. Baus, T. Coussaert, and R. Achrayah, Physica A **232**, 575 (1996).
[42] M. Baus and R. Achrayah, J. Phys.: Condens. Matter **8**, 9633 (1996).
[43] Z. Nemeth, C. N. Likos, and H. Löwen, Magy. Kem. Foly. **102**, 515 (1996).
[44] C. Rascon, E. Velasco, L. Mederos, and G. Navascués, J. Chem. Phys. **106**, 6689 (1997).
[45] N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).
[46] M. S. Wertheim, Phys. Rev. Lett. **10**, 321 (1963).
[47] E. Thiele, J. Chem. Phys. **39**, 474 (1963).
[48] This higher-order critical point has been given different names, which are a matter of some controversy [see J. M. Kincaid and E. D. G. Cohen, Phys. Rep., Phys. Lett. **22C**, 57 (1975); D. Roux, C. Coulon, and M. E. Cates, J. Phys. Chem. **96**, 4174 (1992)]. Since that discussion is not particularly relevant here, we avoided using any of them.
[49] This is not a Landau expansion in the stricter sense, as it is only valid in zero field; its relation to the true Landau expansion will be discussed in the last section.
[50] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 3rd ed. (Pergamon Press, London, 1980), Part 1.
[51] B. J. Alder and T. E. Wainwright, J. Chem. Phys. **27**, 1208 (1957).
[52] P. Tarazona, Mol. Phys. **52**, 81 (1984).
[53] A. D. J. Haymet and D. W. Oxtoby, J. Chem. Phys. **84**, 1769 (1986).
[54] J. Stecki and A. Kloczkowski, Mol. Phys. **42**, 51 (1981).
[55] R. Hołyst and A. Poniewierski, Mol. Phys. **71**, 561 (1990).
[56] W. E. McMullen and D. W. Oxtoby, J. Chem. Phys. **86**, 4146 (1987).
[57] C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids* (Clarendon Press, Oxford, 1984), Vol. 1, Appendix A.
[58] We are grateful to B. M. Mulder for clarifying this point.
[59] This argument is due to M. A. Osipov.
[60] J. Katriel, G. F. Kventsel, G. R. Luckhurst, and T. J. Sluckin, Liq. Cryst. **1**, 337 (1986).