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On the Landau bicritical point for hard biaxial particles

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We consider the isotropic symmetry breaking bifurcations for an arbitrary free energy functional describing hard non-spherical particles. It is shown that a large class of functionals for hard biaxial particle fluids that incorporate excluded volume effects solely through the distribution averaged pair excluded volume all have Landau bicritical points at the same particle shape parameters.

1. Introduction

In a recent paper Hołyst and Poniewierski [1] studied fluids of hard spheroplatelets and hard ellipsoids via the liquid-crystalline version of the smoothed density approximation [2, 3]. Using a bifurcation analysis, previously elaborated in the context of the Onsager mean field approximation by the present author ([4] hereafter referred to as I), they located the lines of Landau bicritical points for these systems, i.e. one parameter families of particles for which the isotropic phase becomes directly unstable to biaxial perturbations rather than to the more symmetric nematic perturbations. They note that the equations fixing the particles which satisfy the Landau bicritical point conditions that result from their analysis are in fact *the same* as in the Onsager case. Furthermore they mention that the same observation also applies to a, suitably altered, version of a density-functional theory for nematics developed by Sin-Doo Lee [5]. These remarks prompted us to investigate the underlying mechanism of these coinciding results. To this end we formulate the first and second order bifurcation equations for an arbitrary density functional describing a homogeneous fluid of hard non-spherical particles and show how these results follow from a rather general assumption concerning the form of the functional employed.

2. The general theory

We start by considering the general form of the free energy per particle of a spatially homogeneous hard particle fluid as a functional of the singlet orientational distribution function $\psi(\Omega)$

$$\beta f[\psi] = \int d\Omega\, \psi(\Omega)\{\ln \psi(\Omega) - 1\} - \Phi[\psi] + \beta f_0. \tag{1}$$

Here the first term is the orientational part of the ideal gas contribution, $\Phi[\psi]$ is the functional describing the excess free energy and f_0 denotes the contributions to the free energy which do not depend on the orientational distribution. Note that for reasons of notational economy we leave the dependence on the particle density ρ understood. Furthermore we introduce the orientational direct correlation functions

$$c^{(n)}[\psi](\Omega_1, \ldots, \Omega_n) = \frac{\delta^{(n)}\Phi[\psi]}{\delta\psi(\Omega_1)\,\delta\psi(\Omega_2)\ldots\delta\psi(\Omega_n)}. \tag{2}$$

These are related to the conventional correlation functions [6] by an integration over the spatial degrees of freedom and the absorption of a factor of ρ^{n-1}. Using these we can immediately write the equation for the normalized distribution for which the functional (1) is stationary as

$$\psi(\Omega) = \frac{\exp\{c^{(1)}[\psi](\Omega)\}}{\int d\Omega' \exp\{c^{(1)}[\psi](\Omega')\}}. \tag{3}$$

The single particle correlation $c^{(1)}[\psi]$ appearing in this equation can be identified as the effective external potential acting on a single particle due to the interactions with the rest of the system. Introducing the isotropic distribution $\psi_0 = 1/8\pi^2$ we have, as a consequence of global rotational invariance, that all of the $c^{(n)}[\psi_0]$ are globally rotationally invariant functions of their orientational arguments. For $c^{(1)}[\psi_0]$ this implies that it is in fact a constant *in*dependent of the orientation Ω. Hence ψ_0 is a solution of equation (3) at any value of the density. To find bifurcating solutions we introduce the expansions

$$\left.\begin{aligned} \rho &= \rho_0 + \rho_1\varepsilon + \rho_2\varepsilon^2 + \dots, \\ \psi(\Omega) &= \psi_0 + \psi_1(\Omega)\varepsilon + \psi_2(\Omega)\varepsilon^2 + \dots, \end{aligned}\right\} \tag{4}$$

around the isotropic solution. Note that because of the normalization of $\psi(\Omega)$ we must have that

$$\int d\Omega \psi_n(\Omega) = \delta_{n,0}. \tag{5}$$

Expanding the one particle direct correlation occurring in equation (3) to second order in ε we find

$$\begin{aligned} c^{(1)}[\psi](\Omega) = {} & c_0^{(1)} + \varepsilon\left\{\rho_1\partial_\rho c_0^{(1)} + \int d\Omega' c_0^{(2)}(\Omega,\Omega')\psi_1(\Omega')\right\} \\ & + \tfrac{1}{2}\varepsilon^2\left\{\rho_1^2\partial_\rho^2 c_0^{(1)} + 2\rho_2\partial_\rho c_0^{(1)} + 2\rho_1\int d\Omega'\partial_\rho c_0^{(2)}(\Omega,\Omega')\psi_1(\Omega')\right. \\ & \left. + 2\int d\Omega' c_0^{(2)}(\Omega,\Omega')\psi_2(\Omega') + \int d\Omega'\int d\Omega'' c_0^{(3)}(\Omega,\Omega',\Omega'')\psi_1(\Omega')\psi_1(\Omega'')\right\}. \end{aligned} \tag{6}$$

Here the ∂_ρ are derivatives with respect to the density and the subscript zero indicates that all functions are evaluated at the isotropic solution ψ_0 with density ρ_0. We have, moreover, assumed that the functional is smooth enough to permit interchange of the partial derivatives with respect to the density with the functional derivatives with respect to the orientational distribution. Inserting the expansions (4) and (5) into the stationarity equation (3) and equating terms left and right of the equal sign with like powers of ε up to order ε^2 yields the equations

$$\psi_1(\Omega) = \frac{1}{8\pi^2}\int d\Omega' c_0^{(2)}(\Omega,\Omega')\psi_1(\Omega') \tag{7}$$

and

$$\begin{aligned}\psi_2(\Omega) \;=\; \frac{1}{8\pi^2}\Bigg\{ & \int d\Omega' c_0^{(2)}(\Omega,\Omega')\,\psi_2(\Omega') + \rho_1 \int d\Omega' \partial_\rho c^{(2)}(\Omega,\Omega')\,\psi_1(\Omega') \\ & + \tfrac{1}{2}\Bigg(\int d\Omega' \int d\Omega'' c_0^{(3)}(\Omega,\Omega',\Omega'')\,\psi_1(\Omega')\,\psi_1(\Omega'') \\ & - \frac{1}{8\pi^2}\int d\Omega' \int d\Omega'' \int d\Omega''' c_0^{(3)}(\Omega',\Omega'',\Omega''')\,\psi_1(\Omega'')\,\psi_1(\Omega''')\Bigg) \\ & + \tfrac{1}{2}\Bigg(\left(\int d\Omega' c_0^{(2)}(\Omega,\Omega')\,\psi_1(\Omega')\right)^2 \\ & - \frac{1}{8\pi^2}\int d\Omega' \left(\int d\Omega'' c_0^{(2)}(\Omega',\Omega'')\,\psi_1(\Omega'')\right)^2\Bigg)\Bigg\}. \qquad (8)\end{aligned}$$

3. Average excluded volume dependent functionals

We now specialize to the class of theories in which the excess free energy depends on the singlet orientational distribution function only through the distribution average of the pair excluded volume at fixed relative orientation. We describe this dependence through the quantity

$$\mathscr{E}[\psi] \;=\; \tfrac{1}{2}\int d\Omega' \int d\Omega''\, V(\Omega',\Omega'')\,\psi(\Omega')\,\psi(\Omega''), \qquad (9)$$

where $V(\Omega,\Omega')$ is the pair excluded volume at fixed relative orientation. $\mathscr{E}[\psi]$ is in fact the second virial coefficient in the density expansion. The general form of the excess part of the free energy functional for the class of theories we want to consider can then be written as

$$\Phi[\psi] \;=\; \phi(\rho, \mathscr{E}[\psi]), \qquad (10)$$

here ϕ is a two variable function that has to be specified to obtain a particular theory. The direct correlation functions appearing in the bifurcation equations (7) and (8) are now expressed as

$$\left.\begin{aligned} c_0^{(2)}(\Omega,\Omega') &= V_0^2\partial_{\mathscr{E}}^2\phi_0 + \partial_{\mathscr{E}}\phi_0\, V(\Omega,\Omega'), \\ c_0^{(3)}(\Omega,\Omega',\Omega'') &= V_0^3\partial_{\mathscr{E}}^3\phi_0 + V_0\partial_{\mathscr{E}}^2\phi_0\{V(\Omega,\Omega') + V(\Omega,\Omega'') + V(\Omega',\Omega'')\}, \end{aligned}\right\} \qquad (11)$$

where we have introduced the unweighted rotational average of the pair excluded volume

$$V_0 \;=\; \left(\frac{1}{8\pi^2}\right)^2 \int d\Omega' \int d\Omega''\, V(\Omega',\Omega''). \qquad (12)$$

Insertion into equations (7) and (8) and using equation (5) yields the bifurcation equations

$$\psi_1(\Omega) \;=\; \frac{\partial_{\mathscr{E}}\phi_0}{8\pi^2}\int d\Omega' V(\Omega,\Omega')\,\psi_1(\Omega') \qquad (13)$$

and

$$\psi_2(\Omega) = \frac{1}{8\pi^2}\left\{\partial_{\mathscr{E}}\phi_0 \int d\Omega' V(\Omega,\Omega')\psi_2(\Omega') + \rho_1\partial_\rho\partial_{\mathscr{E}}\phi_0 \int d\Omega' V(\Omega,\Omega')\psi_1(\Omega') + \tfrac{1}{2}(\partial_{\mathscr{E}}\phi_0)^2\left(\left(\int d\Omega' V(\Omega,\Omega')\psi_1(\Omega')\right)^2 - \frac{1}{8\pi^2}\int d\Omega' \left(\int d\Omega'' V(\Omega',\Omega'')\psi_1(\Omega'')\right)^2\right)\right\}, \tag{14}$$

valid in our restricted class of theories. The structure of these equations is identical to that in the Onsager mean field case I, the latter being exactly reproduced by inserting the explicit form of the excess free energy

$$\phi_{\text{Onsager}}(\rho, \mathscr{E}[\psi]) = -\rho\mathscr{E}[\psi]. \tag{15}$$

The comparison shows that up to this order in the bifurcation expansion the dependence on the specific functional enters only through the definition of the coefficients multiplying the integrals in equations (13) and (14). Following the analysis outlined in I we see that these coefficients

$$\lambda_1 = \partial_{\mathscr{E}}\phi_0, \quad \lambda_2 = \rho_1\partial_\rho\partial_{\mathscr{E}}\phi_0 \tag{16}$$

determine the location where and the slope with which the bifurcating solution branches off from the isotropic solution, respectively. In the determination of the location of the Landau bicritical points for biaxially symmetric particles the absolute value of these coefficients plays no role. These points are determined solely by the coefficients in an invariant expansion of the pair excluded volume at fixed relative orientation. We therefore arrive at the desired result. *Any theory that describes orientational ordering effects of hard non-spherical particles through a functional of the type* (10) *will predict Landau bicritical points for biaxially symmetric particles at universal values of the particle shape parameters determined by the pair excluded volume only.* For completeness we give the recipe for obtaining the bicritical points in the Appendix.

Intuitively this result can be understood by considering the fact that the existence of the bicritical points is essentially due to the symmetries of the effective interaction between the particles. In the class of theories considered here all symmetry related information is coded into the functional $\mathscr{E}[\psi]$ which in turn is completely determined by the pair excluded volume $V(\Omega, \Omega')$. In the general case there will also be n particle (with $n \geqslant 2$) contributions to the effective interaction which will give rise to a non-trivial three particle correlation $c_0^{(3)}$ appearing in the second order bifurcation equation (8). The location of the bicritical points is then expected to depend also on the relative strength of the two and three particle contributions which in general will depend on the density.

The simplest model in which we could study the effect of these higher order effects would be the functional obtained by truncating the virial series after the third order term, i.e. add the third virial coefficient to the Onsager model. Unfortunately no explicit expressions exist for the probability of simultaneous overlap of three non-spherical particles with fixed orientations which is the quantity that enters as a kernel in the definition of the third virial coefficient [7]. Moreover in this case we would be able again to locate the Landau points independently of the bifurcation density as the last two terms in equation (8) share a common density dependent factor of ρ_0^2 since, in this case, both $c_0^{(2)}$ squared and $c_0^{(3)}$ are proportional to the square of the density.

In any case equations (7) and (8) can be used to obtain a formal solution of the problem in the general case by considering the invariant expansions of the relevant direct correlations. The location of the bifurcation points as well as the conditions for the bicritical points will then be expressed in terms of the density dependent coefficients appearing in these invariant expansions.

Appendix

In this Appendix we collect the formulas for locating the bifurcation points as well as the Landau bicritical points for density functionals of the type (10) as applied to systems with biaxially symmetric particles. Details of the definitions as well as a deviation of the results can be found in I.

The pair excluded volume of two biaxially symmetric particles is expanded as

$$K(\Omega,\Omega') = \sum_{l,m,n} \frac{(2l+1)}{8\pi^2} K_{l,mn}\Delta^{(l)}_{m,n}(\Omega'^{-1}\Omega), \qquad \text{(A 1)}$$

where the symmetry adapted set of orthogonal functions $\Delta^{(l)}_{m,n}(\tilde{\Omega})$ is defined in terms of the standard rotation matrices [8] through

$$\Delta^{(l)}_{m,n}(\tilde{\Omega}) = (\tfrac{1}{2}\sqrt{2})^{2+\delta_{m,0}+\delta_{n,0}} \sum_{\sigma,\sigma'=\{-1,1\}} \mathfrak{D}^{(l)}_{\sigma m,\sigma' n}(\tilde{\Omega}); \quad l\text{: even}; \quad 0 \leqslant m, n \leqslant l\text{: even}. \qquad \text{(A 2)}$$

Their explicit form in terms of the standard Euler angles (α, β, γ) for the case $l = 2$ is

$$\left.\begin{aligned} \Delta^{(2)}_{0,0}(\Omega) &= \tfrac{1}{2}(3\cos^2\beta - 1), \\ \Delta^{(2)}_{0,2}(\Omega) &= \tfrac{1}{2}\sqrt{3}\sin^2\beta\cos 2\gamma, \\ \Delta^{(2)}_{2,0}(\Omega) &= \tfrac{1}{2}\sqrt{3}\sin^2\beta\cos 2\alpha, \\ \Delta^{(2)}_{2,2}(\Omega) &= \tfrac{1}{2}(1+\cos^2\beta)\cos 2\alpha\cos 2\gamma - \cos\beta\sin 2\alpha\sin 2\gamma. \end{aligned}\right\} \qquad \text{(A 3)}$$

The bifurcation density can be determined from the implicit equation for ρ_0

$$\partial_g\phi(\rho_0, \tfrac{1}{2}(8\pi^2)\rho_0^2 V_0) = -\frac{8\pi^2}{\kappa_*}, \qquad \text{(A 4)}$$

where κ_* is determined by the expansion coefficients of the pair excluded volume (A 1) with $l = 2$

$$\kappa_* = \tfrac{1}{2}(K_{2,00} + K_{2,22}) - \tfrac{1}{2}\{(K_{2,00} - K_{2,22})^2 + 4K^2_{2,02}\}^{1/2}. \qquad \text{(A 5)}$$

The Landau bicritical points are determined by the two equations

$$\left.\begin{aligned} K_{2,02} &= 0 \quad \text{and} \quad K_{2,00} - K_{2,22} > 0, \\ K_{2,00} - K_{2,22} &= \frac{-|K_{2,02}|}{\tfrac{1}{2}\sqrt{3}}, \end{aligned}\right\} \qquad \text{(A 6)}$$

which implicitly specify certain values for the parameters describing the actual shape of the particles considered.

References

[1] Hołyst, R., and Poniewierski, A., 1990, *Molec. Phys.*, **69**, 193.
[2] Poniewierski, A., and Hołyst, R., 1988, *Phys. Rev. Lett.*, **61**, 2461.

[3] HOŁYST, R., and PONIEWIERSKI, A., 1989, *Phys. Rev.* A, **39**, 2742.
[4] MULDER, B. M., 1989, *Phys. Rev.* A, **39**, 360.
[5] LEE, S. D., 1987, *J. chem. Phys.*, **87**, 4972.
[6] EVANS, R., 1979, *Adv. Phys.*, **28**, 143.
[7] MULDER, B. M., and FRENKEL, D., 1985, *Molec. Phys.*, **55**, 1193.
[8] BRINK, D. M., and SATCHLER, G. R., 1962, *Angular Momentum* (Oxford University Press).