Supplementary Material (ESI) for Soft Matter

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December 30, 2009

Supplementary Data: Critical points of the homogeneous free energy equation

The homogeneous form of the full free energy:

$$\begin{aligned} f - f_0 &= \frac{1}{2}a\left(\boldsymbol{Q}:\boldsymbol{Q}\right) - \frac{1}{3}b\left(\boldsymbol{Q}\cdot\boldsymbol{Q}\right):\boldsymbol{Q} + \frac{1}{4}c\left(\boldsymbol{Q}:\boldsymbol{Q}\right)^2 \\ &+\frac{1}{2}\alpha\left|\Psi\right|^2 + \frac{1}{4}\beta\left|\Psi\right|^4 \\ &-\frac{1}{2}\delta\left|\Psi\right|^2\left(\boldsymbol{Q}:\boldsymbol{Q}\right) - \frac{1}{2}e\boldsymbol{Q}:\left(\boldsymbol{\nabla}\Psi\right)\left(\boldsymbol{\nabla}\Psi^*\right) \\ &+\frac{1}{2}l_1\left(\boldsymbol{\nabla}\boldsymbol{Q}\right)^2 + \frac{1}{2}l_2\left(\boldsymbol{\nabla}\cdot\boldsymbol{Q}\right)^2 \\ &+\frac{1}{2}l_3\boldsymbol{Q}:\left(\nabla\boldsymbol{Q}:\nabla\boldsymbol{Q}\right) \\ &+\frac{1}{2}b_1\left|\boldsymbol{\nabla}\Psi\right|^2 + \frac{1}{4}b_2\left|\nabla^2\Psi\right|^2 \end{aligned} \tag{1}$$

$$a = a_0(T - T_{NI}); \alpha = \alpha_0(T - T_{AI})$$

is derived assuming an ideal smectic-A phase where the tensorial and complex order parameters take the form:

$$\boldsymbol{Q} = S\left(\boldsymbol{xx} - \frac{1}{3}\boldsymbol{I}\right) + \frac{1}{3}P\left(\boldsymbol{yy} - \boldsymbol{zz}\right) \tag{2}$$

$$\Psi = \psi e^{iqx} \tag{3}$$

where $\boldsymbol{x}/\boldsymbol{y}/\boldsymbol{z}$ are the coordinate axes and $q = \frac{2\pi}{d}$ is the magnitude of the smectic-A density wave vector. Substituting eqns. 2-3 into eqn. 1 and simplifying yields the homogeneous free energy density:

$$\begin{aligned} f(S, P, \psi, q, T) &= \frac{1}{3}a\left(S^2 + \frac{1}{3}P^2\right) - \frac{2}{27}bS\left(S^2 - P^2\right) + \frac{1}{9}c\left(S^2 + \frac{1}{3}P^2\right)^2 \\ &+ \frac{1}{2}\alpha\psi^2 + \frac{1}{4}\beta\psi^4 - \frac{1}{3}\delta\psi^2\left(S^2 + \frac{1}{3}P^2\right) \\ &+ \frac{1}{2}b_1\psi^2q^2 + \frac{1}{4}b_2\psi^2q^4 - \frac{1}{3}eS\psi^2q^2 \end{aligned} \tag{4}$$

a function of four scalar order parameters and temperature. By parameterization of the homogeneous free energy (neglecting biaxiality), the critical values of eqn. 4 can be determined using the requirement of the first derivatives equaling

0:

$$\frac{\partial f}{\partial S} = \frac{12cS^3 - 6bS^2 + \left(4cP^2 - 18\delta\psi^2 + 18a\right) S + 2bP^2 - 9e\psi^2 q^2}{27} \quad (5)$$

$$\frac{\partial f}{\partial P} = \frac{12cPS^2 + 12bPS + 4cP^3 + \left(18a - 18\delta\psi^2\right) P}{81} \quad (6)$$

$$\frac{\partial f}{\partial \psi} = -\frac{12\delta\psi S^2 + 12e\psi q^2 S + 4\delta\psi P^2 - 9b_2\psi q^4 - 18b_1\psi q^2 - 18\beta p^3 - 18\alpha\psi}{18} \quad (7)$$

$$\frac{\partial f}{\partial q} = -\frac{2e\psi^2 qS - 3b_2\psi^2 q^3 - 3b_1\psi^2 q}{3} \quad (8)$$

Using the resulting equation system eqn. 5-8, critical values of the homogeneous free energy eqn. 4 can be determined by assuming the existence of different liquid crystalline states:

1. *Uniaxial nematic*: $S \neq 0; P, \psi, q = 0$, these assumptions result in the solution of the standard nematic equations:

$$S = \pm\frac{\sqrt{b^2 - 24ac} - b}{4c}; S = 0 \quad (9)$$

2. *Biaxial nematic*: $S, P \neq 0; \psi, q = 0$:

$$S = -\frac{\sqrt{b^2 - 24ac} + b}{8c}$$

$$P = \frac{\sqrt{3}\sqrt{-2S^2 - \frac{2bS}{c} - \frac{3a}{c}}}{\sqrt{2}} \quad (10)$$

3. *Uniaxial smectic-A*: $S, \psi, q \neq 0; P = 0$, where the roots of eqn. 11 must be numerically determined:

$$0 = 4AS^3 + 3BS^2 + 2CS + D \quad (11)$$

$$A = -\left(16e^4 + 96b_2\delta e^2 + 144b_2^2\delta^2 - 144b_2^2\beta c\right)\left(1296b_2^2\beta\right)^{-1}$$

$$B = -\left(-96b_1e^3 - 288b_1b_2\delta e + 96bb_2^2\beta\right)\left(1296b_2^2\beta\right)^{-1}$$

$$C = -\left(\left(216b_1^2 - 144\alpha b_2\right)e^2 + \left(216b_1^2b_2 - 432\alpha b_2^2\right)\delta - 432ab_2^2\beta\right)\left(1296b_2^2\beta\right)^{-1}$$

$$D = -\left(432\alpha b_1b_2 - 216b_1^3\right)e\left(1296b_2^2\beta\right)^{-1}$$

$$q^2 = \frac{2eS - 3b_1}{3b_2} \quad (12)$$

$$\psi^2 = \frac{4\delta S^2 + 4eSq^2 - 3b_2q^4 - 6b_1q^2 - 6\alpha}{6\beta} \quad (13)$$

4. *Biaxial smectic-A*: $S, P, \psi, q \neq 0$, where the same numerical procedure as

used for the uniaxial smectic solution can be used used:

$$\begin{aligned} 0 &= (64ce^4S^3 + 3\left(-96b_1ce^3 - 96bb2\delta e^2 - 384\,b\,b2^2\,de^2 + 384\,b\,b2^2\,be\,c\right)S^2 \\ &+ 2\left(\left(\left(216{b_1}^2 - 144alb_2\right)c - 144ab_2\delta\right)e^2 + 288bb_1b_2\delta e + 144b^2{b_2}^2\,be\right)S \\ &+ \left(432ab_1b_2\delta + \left(432\alpha b_1b_2 - 216{b_1}^3\right)c\right)e + \left(432\alpha b{b_2}^2 - 216b{b_1}^2b_2\right)\delta \\ &+ 432ab{b_2}^2\beta)/(1296{b_2}^2\delta^2 - 1296{b_2}^2\beta c) \qquad (14) \\ P^2 &= (-((4\delta e^2 + 12b_2\delta^2 - 12b_2\beta c)S^2 + (-12b_1\delta e - 12bb_2\beta)S + (9b_1^2 - 18\alpha b_2)\delta \\ &- 18ab_2\beta))/((4b_2\delta^2 - 4b_2\beta c) \qquad (15) \\ \psi^2 &= ((4e^2 + 12b_2\delta)S^2 - 12b_1eS + 4b_2\delta P^2 - 18\alpha b_2 + 9b_1^2)/(18b_2\beta) \qquad (16) \\ q^2 &= (2eS - 3b_1)/(3b_2) \qquad (17) \end{aligned}$$

Finally, solutions from all four states (uniaxial/biaxial nematic and uniaxial/biaxial smectic-A) must be classified and imaginary solutions discarded. Critical point values can be classified by computationally determining the Hessian matrix of eqn. 4 associated with each solution:

$$H_{ij} = \frac{\partial^2 f}{\partial i \partial j} \qquad (18)$$

where $i, j = \{S, P, \psi, q\}$ and the determinant of the Hessian matrix is used to classify the critical value.