MAMA/344, NST3AS/344, MAAS/344

MAT3 MATHEMATICAL TRIPOS Part III

Friday 13 June 2025 $\,$ 9:00 am to 11:00 am $\,$

PAPER 344

THEORETICAL PHYSICS OF SOFT CONDENSED MATTER

Before you begin please read these instructions carefully

Candidates have TWO HOURS to complete the written examination.

Attempt no more than **TWO** questions. There are **THREE** questions in total. The questions carry equal weight.

STATIONERY REQUIREMENTS

Cover sheet Treasury tag Script paper Rough paper

SPECIAL REQUIREMENTS None

You may not start to read the questions printed on the subsequent pages until instructed to do so by the Invigilator. 1 (a) For a closed system comprising a binary fluid mixture of two species, briefly say what is meant by the compositional order parameter $\phi(\mathbf{r})$. In what sense this is 'conserved'? Write down the Landau Ginzburg free energy $F[\phi]$, and explain why a linear term in ϕ has no effect.

(b) Consider a binary fluid in which one of the species (only) can show polar ordering of molecular orientations. For the purposes of this question, the polar order parameter can be viewed as a scalar $p(\mathbf{r})$, as would anyway be true in one dimension. The following free energy functional can be used to describe such a system:

$$F[\phi, p] = \int \left\{ \frac{a}{2}\phi^2 + \frac{b}{4}\phi^4 + \frac{\kappa_1}{2}(\nabla\phi)^2 + \frac{c}{2}\phi p^2 + \frac{A}{2}p^2 + \frac{B}{4}p^4 + \frac{\kappa}{2}(\nabla p)^2 \right\} d\mathbf{r}.$$

Show that (i) the coupling term $\frac{c}{2}\phi p^2$ cannot be ignored despite being linear in ϕ ; (ii) the coupling constant c can be chosen positive without loss of generality. Also, give physical reasons why (iii) there is no term in ϕp ; and (iv) b and B cannot be negative.

(c) Explain why, at mean field level (uniform ϕ, p) one may construct for the conserved variable ϕ a free energy density $F/V = f(\phi)$ by unconstrained minimization over p. Taking positive c, show that the result is

$$f(\phi) = \frac{a}{2}\phi^2 + \frac{b}{4}\phi^4 - \frac{C}{2}(\phi - \phi_o)^2\theta(\phi_o - \phi)$$

where $\theta(x) \equiv \frac{1}{2} \left(\frac{|x|}{x} + 1 \right)$ is the Heaviside function, and C and ϕ_o are constants, which you should find in terms of the parameters in $F[\phi, p]$. Interpret ϕ_o .

- (d) Restricting attention to parameter choices with a > 0 and for which $\phi_o = 0$:
 - (i) Sketch $f(\phi)$ and show that the system will phase separate for $C > C_c$, giving the value of C_c .
 - (ii) Explain a graphical construction on $f(\phi)$ that determines the two binodal densities ϕ_1, ϕ_2 . Alternatively and for equal credit, construct but do not solve two simultaneous equations for ϕ_1, ϕ_2 by equating chemical potential and pressure in the two phases. Is this mean-field phase transition continuous or discontinuous?

(e) Now consider $F[\phi, p]$ for case $b = \kappa_1 = 0$. Here the ϕ field can be eliminated by Gaussian integration to give a free energy function F[p] that governs the statistics of $p(\mathbf{r})$.

(i) Assuming that the result of the Gaussian integration can also be found by setting $\frac{\delta F[\phi,p]}{\delta\phi(\mathbf{r})} = 0$, show that

$$F[p] = \int \left\{ \frac{A}{2}p^2 + \frac{\tilde{B}}{4}p^4 + \frac{\kappa}{2}(\nabla p)^2 \right\} d\mathbf{r}$$

with $\tilde{B} = B - \frac{c^2}{2a}$. Further assuming that A > 0 and that \tilde{B} is negligible, identify the functional form of the correlator $S_p(q) \equiv \langle p_{\mathbf{q}} p_{-\mathbf{q}} \rangle$ at Fourier wavevector \mathbf{q} .

(ii) Denoting the Fourier transform of $S_p(q)$ by $C_p(r)$, say what you can about the likely functional form of the real-space correlator for the ϕ field, $C_{\phi}(r) \equiv \langle \phi(\mathbf{0})\phi(\mathbf{r})\rangle - \langle \phi \rangle^2$. (You are not asked to calculate $C_p(r)$ or $C_{\phi}(r)$ explicitly.)

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2 (a) Starting from a suitable Landau Ginzburg free energy $F = \int \{f(\phi) + \kappa (\nabla \phi)^2 / 2\} d\mathbf{r}$, and stating any assumptions you make, derive the hydrodynamic (noiseless) equations of Model B in the form

$$\begin{split} \dot{\phi} &= -\nabla \cdot \mathbf{J}, \\ \mathbf{J} &= -M \nabla (a\phi + b\phi^3 - \kappa \nabla^2 \phi). \end{split}$$

(b) Show by considering force balance on a 3D spherical droplet of (large) radius R with positive ϕ , in coexistence with a surrounding phase of negative ϕ , that the coexistence condition is $\phi = \pm \phi_B + \delta$ where $\phi_B = (-a/b)^{1/2}$, and $\delta = \lambda/R$ where $\lambda = \frac{\sigma}{\alpha \phi_B}$ with $\alpha = f''(\phi_B)$ and σ the interfacial tension.

(c) Briefly explain why, if the bulk phase has $\phi = -\phi_B$ far from the droplet (rather than $\phi = -\phi_B + \delta$), the droplet will slowly evaporate. Show that, writing $\phi = -\phi_B + g(\mathbf{r})$ in the exterior region and taking a quasi-static approximation, one has $\nabla^2 g = 0$ with boundary conditions $g = \delta$ at the droplet surface and g = 0 at infinity. Show also that the current normal to the droplet surface is $J_n = -M\alpha\nabla_n g$, with ∇_n a derivative in the normal direction. Show further that the normal velocity of the interface obeys $v_n = -\frac{J_n}{2\phi_B}$.

(d) Now consider a flat interface in the horizontal (x, y) plane between bulk coexisting phases arranged so that $\phi \to \mp \phi_B$ for $z \to \pm \infty$, which is perturbed by a small height perturbation h(x, y) in the z direction. Assume that the same quasi-static approximation holds with boundary condition $g(x, y, 0) = -\frac{\sigma K}{2\alpha\phi_B}$, where K(x, y) is the interfacial mean curvature. Noting that to leading order in small $h, K = (\partial_x^2 + \partial_y^2)h$, solve $\nabla^2 g = 0$ in the upper half space for a sinusoidal height perturbation $h = \eta \sin(qx)$. Hence find the normal current $J_n(x, y, z)$ at $z = 0^+$.

(e) Supposing this current to be the only contribution to $v_n = \dot{h}$, show that $\dot{\eta} = -\nu |q|^3 \eta$ and find the constant ν . Confirm that $\nu > 0$, give a brief physical argument for its sign. The nonanalytic decay rate $\eta |q|^3$ at low q is a signature of nonlocal dynamics for h(x, y). Explain why this arises here.

(f) In practice the above calculation for ν gives *half* the correct value. Why?

3 For a polar liquid crystal with order parameter $\mathbf{p}(\mathbf{r}, t)$ the law of advection is

$$\frac{D\mathbf{p}}{Dt} = (\partial_t + \mathbf{v} \cdot \nabla)\mathbf{p} + \mathbf{\Omega} \cdot \mathbf{p} - \xi \mathbf{D} \cdot \mathbf{p}$$
(1)

where Ω and **D** are respectively the antisymmetric and symmetric parts of the velocity gradient tensor $\nabla_i v_j$. Here ξ is a material-dependent parameter.

(a) Without detailed calculations, explain why the coefficient of the Ω term must be unity, as written, rather than a second material-dependent parameter.

(b) By considering the advective free energy increment in a small incompressible displacement $\mathbf{u} = \mathbf{v}\Delta t$, show that the stress tensor $\Sigma_{ij}^{p}(\mathbf{r})$, caused by the polar order parameter, obeys $\Sigma_{ij}^{p} = \Sigma_{ij}^{(1)} + \Sigma_{ij}^{(2)} + \Sigma_{ij}^{(3)}$, where

$$\nabla_i \Sigma_{ij}^{(1)} = -p_i \nabla_j h_i$$

$$\Sigma_{ij}^{(2)} = (p_i h_j - p_j h_i)/2$$

$$\Sigma_{ij}^{(3)} = \xi(p_i h_j + p_j h_i)/2$$

with $\mathbf{h}(\mathbf{r}) \equiv \delta F / \delta \mathbf{p}(\mathbf{r})$ the molecular field.

(c) A certain laboratory device is designed to create an incompressible, uniaxial extensional flow in three dimensions. This is a uniform flow field $\mathbf{v}(x, y, z)$ for which $\mathbf{\Omega} = \mathbf{0}$ and \mathbf{D} is diagonal in (x, y, z) axes with eigenvalues $D_{xx} = \gamma$, $D_{yy} = D_{zz} = -\gamma/2$.

- (i) Assuming that **p** remains uniform in space, and is governed by the usual hydrodynamic equation of motion $D\mathbf{p}/Dt = -\Gamma\mathbf{h}$, show that the effect of the flow is to shift $\mathbf{h} \to \tilde{\mathbf{h}} \equiv \mathbf{h} + \alpha(p_x, -p_y/2, -p_z/2)$ and find the constant α .
- (ii) Taking the free energy density for uniform states to be $\mathbb{F} = \frac{a}{2}p^2 + \frac{b}{4}p^4$ with b > 0, find a modified free energy of the form $\mathbb{F}_{\text{mod}} = \frac{1}{2}p_iA_{ij}p_j + \frac{b}{4}p^4$ describing the system under uniform flow conditions. (You are not asked to go beyond mean field theory.) For each sign of α , identify from \mathbb{F}_{mod} the character of the phase transition whereupon **p** first becomes nonzero on decreasing *a* and find the critical value a_c and p(a). In each case include a careful statement of what symmetry gets spontaneously broken at the ordering transition.
- (iii) For the case with $\alpha < 0$ and in the ordered phase, find the order parameter stress Σ_{ij}^p in the flowing system.

END OF PAPER

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