UNIVERSITY OF CAMBRIDGE

MAMA/344, NST3AS/344, MAAS/344

MAT3

MATHEMATICAL TRIPOS Part III

Monday, 12 June, 2023 1:30 pm to 3:30 pm

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 system has a conserved scalar order parameter ϕ representing a composition field. Its free energy functional is $F[\phi] = \int \mathbb{F}\, d\mathbf{r}$ with $\mathbb{F} = f(\phi) + \frac{\kappa}{2}(\nabla\phi)^2$, where $f = \frac{a}{2}\phi^2 + \frac{b}{4}\phi^4$ with $a < 0$ and $b, \kappa > 0$.

(a) By considering the change in F caused a small deformation $\mathbf{r} \to \mathbf{r} + \mathbf{u}$, and comparing this to $\int \Sigma_{ij}\varepsilon_{ij}\, d\mathbf{r}$, where Σ_{ij} is the stress tensor and and $\varepsilon_{ij} = \nabla_i u_j$ is the strain tensor, derive the result that

$$\nabla_i \Sigma_{ij} = -\phi \nabla_j \mu \qquad (1)$$

where the chemical potential is defined via $\mu(\mathbf{r}) = \delta F/\delta\phi(\mathbf{r})$.

Note: For full credit, do not assume the deformation is incompressible. For partial credit, you may assume this.

(b) Verify that (1) is obeyed by the following expression for the stress tensor (which you are not asked to prove)

$$\Sigma_{ij} = -\Pi\, \delta_{ij} - \kappa(\nabla_i\phi)(\nabla_j\phi) \qquad (2)$$

where $\Pi = \mu\phi - \mathbb{F}$.

(c) Explain why $\mu(\mathbf{r})$ is independent of $\mathbf{r}$ for a system in equilibrium. Explain further why it vanishes in the case of a phase separation between bulk phases with densities $\pm\phi_B$ where $\phi_B = \sqrt{-a/b}$. Hence find a nonlinear ODE for the interfacial profile $\phi(x)$, where x is a coordinate normal to the interface between two such phases.

(d) Writing $\phi(x) = \phi_B g(u)$ with $u = x/\xi_0$ and $\xi_0^2 = -2\kappa/a$, derive that the solution of the required ODE is $\phi(x) = \pm\phi_B \tanh[(x - x_0)/\xi_0] \equiv \pm\phi_E(x, x_0)$ where x_0 is a constant of integration that sets the interfacial position.

Note: For partial credit, prove the result by substitution instead.

(e) Without evaluating explicitly the interfacial tension σ, briefly explain why this can be found from the equilibrium profile $\phi(\mathbf{r}) = \phi_E(x)$ via $\sigma A = F[\phi_E] - V f(\phi_B)$ where A and V are the interfacial area and system volume respectively.

(f) Assume without proof the following alternative expression for the interfacial tension:

$$\sigma = \int_{-\infty}^{\infty} [\Sigma_{yy} - \Sigma_{xx}]\, dx \qquad (3)$$

where y is any coordinate perpendicular to the interface normal x. Using (2) and the fact that $\int_{-\infty}^{\infty} \frac{du}{\cosh^4(u)} = 4/3$, show that $\sigma = \sqrt{\frac{-8a^3\kappa}{9b^2}}$.

2 (a) Briefly explain the distinction between polar and nematic liquid crystals, and the order parameters used to describe them.

(b) A certain system of volume V with a vector order parameter $\mathbf{p} = (p_x, p_y, p_z)$ in three dimensions has the free energy functional $F[\mathbf{p}] = \int \mathbb{F}\, d\mathbf{r}$ where

$$\mathbb{F} = \frac{a}{2}|\mathbf{p}|^2 + \frac{b}{4}|\mathbf{p}|^4 + \frac{\kappa}{2}(\nabla_i p_j)(\nabla_i p_j) + \frac{\gamma}{2}|\nabla^2 \mathbf{p}|^2$$

where $p = |\mathbf{p}|$. Treating this system at Gaussian level ($b = 0$) and writing the free energy in Fourier space as

$$F = \frac{1}{2}\sum_{\mathbf{q}} G(q)|\mathbf{p}(q)|^2\,,$$

find $G(q)$. For the case with $\kappa < 0$ and $\gamma > 0$, find the critical value of $a = a_c(\kappa, \gamma)$ for which the fluctuations in $\mathbf{p}$ first become unbounded on decreasing a, and the critical wavenumber q_0 for which this happens.

(c) Suppose that the system for $a < a_c$ forms a 'polar smectic' phase in which the order parameter $\mathbf{p}(x) \equiv p(x)\hat{\mathbf{p}}(x)$ varies along one spatial coordinate only (chosen as the x direction without loss of generality). Two candidate structures are (i) $\hat{\mathbf{p}}$ is fixed, while $p = p_0 \cos q_0 x$, and (ii) $p = p_0$ is fixed, while $\hat{\mathbf{p}} = (0, \cos q_0 x, \sin q_0 x)$ rotates in the plane perpendicular to x.

Show that at mean field level (*i.e.*, ignoring fluctuations about the candidate structure) the free energy of case (i) obeys

$$\frac{F}{V} = \frac{\hat{a}}{4}p_0^2 + \frac{3b}{32}p_0^4$$

where $\hat{a} = a - a_c$, and minimize over p_0 to find $F(a, b, \kappa, \gamma)$ for this structure. Show that the transition from zero to finite p_0 is continuous at the mean-field level considered here.

[*Note:* You may use without proof the fact that $\frac{1}{2\pi}\int_0^{2\pi}(\cos u)^4\, du = 3/8$.]

(d) Perform the same procedure for candidate (ii) and show that for $a < a_c$ the resulting free energy is always 50% more negative than case (i).

(e) By using symmetry arguments (and avoiding further explicit evaluations of F) show that the same free energy as case (ii) is recovered even when the plane of rotation of $\hat{\mathbf{p}}$ is not perpendicular to x, *i.e.* $\hat{\mathbf{p}} = \mathcal{R}(0, \cos q_0 x, \sin q_0 x)$ where $\mathcal{R}$ is any constant rotation matrix (that is, any fixed element of SO(3)).

(f) How would this degeneracy be affected by adding a small term $\lambda|\nabla.\mathbf{p}|^2$ to $\mathbb{F}$? Give a brief but reasoned answer that considers both signs of λ.

3 Consider a phase-separating symmetric binary fluid mixture with conserved order parameter ϕ obeying Model B dynamics without noise in three dimensions:

$$\dot{\phi} = -\nabla.\mathbf{J} \ ; \ \mathbf{J} = -M\nabla\left(\frac{\delta F}{\delta \phi}\right) .$$

Here M is a constant mobility; $F[\phi] = \int \mathbb{F}\, d\mathbf{r}$ with $\mathbb{F} = f(\phi) + \frac{\kappa}{2}(\nabla\phi)^2$ and $f = \frac{a}{2}\phi^2 + \frac{b}{4}\phi^4$ where $a < 0$ and $b, \kappa > 0$. A large spherically symmetric droplet of radius R and composition $\phi = +\phi_B + \mathcal{O}(1/R)$ is immersed in a region whose composition far from the droplet is $\phi(r) = -\phi_B + \tilde{\phi}(r)$ where $\tilde{\phi}(\infty) = \varepsilon > 0$ is the supersaturation. Here $\pm\phi_B$ are the bulk coexistence densities.

(a) By considering the Laplace pressure across a curved interface, or otherwise, explain why local equilibrium at the droplet surface requires $\phi(R^{\pm}) = \mp\phi_B + \delta(R)$, with $\delta(R) \propto \sigma/R$, where σ is the interfacial tension.

Note: You are *not* asked to derive the full result: $\delta(R) = \sigma/(\alpha\phi_B R)$ with $\alpha = f''(\phi_B)$. However this expression *is* needed in part (d) below.

(b) Show that, for small supersaturation and large R, the Model B equations for $\tilde{\phi}(r)$ in the exterior region reduce in the quasistatic limit to the Laplace equation.

(c) Solving this equation, and calculating the radial current $J(r = R^+)$ at the droplet surface, derive the following equation of motion for the droplet radius R:

$$\dot{R} = \frac{1}{2\phi_B}\left(\frac{\alpha M}{R}(\varepsilon - \delta(R))\right)$$

Sketch the right hand side as a function of R. What is the physical significance of $R^*(\varepsilon)$, defined via $\delta(R^*) = \varepsilon$?

(d) Show that the equation for $\dot{R}$ can be rewritten

$$\dot{R} = -\mathcal{M}(R)\, dF/dR \tag{1}$$

where $\mathcal{M} = M/(16\pi\phi_B^2 R^3)$ and $F(R) = 4\pi R^2\sigma - \frac{4}{3}\pi R^3\Delta$ with $\Delta = 2\phi_B\alpha\varepsilon$.

Viewing R as a coarse-grained coordinate with mobility $\mathcal{M}(R)$, interpret the result for the free energy of the droplet $F(R)$. Confirm that F has a maximum at R^* and calculate its value, F^*.

(e) Explain why, when thermal fluctuations are allowed for, Equation (1) should be replaced by a Langevin equation. Approximating $\mathcal{M}$ with a constant value $\overline{\mathcal{M}} \equiv \mathcal{M}(R^*)$, and assuming the Langevin equation then to take the form

$$\dot{R} = -\overline{\mathcal{M}}\, dF/dR + A\,\Lambda\,, \tag{2}$$

with Λ unit white noise, state how (and, briefly, why) the noise amplitude A depends on temperature T and mobility $\overline{\mathcal{M}}$.

(f) Consider a metastable system at supersaturation ε and temperature T, whose volume is such that of order one subcritical ($R \leqslant R^*$) droplet is typically present. Without detailed calculation, give a reasoned estimate of how the time taken for a macroscopic droplet to appear depends on F^*.

END OF PAPER