UNIVERSITY OF CAMBRIDGE

MATHEMATICAL TRIPOS Part III

Monday, 6 June, 2022 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 *Answer all parts of the question.*

A simple model of a symmetric binary fluid in the presence of surfactants has the following free energy functional:

$$F[\phi, \mathbf{p}] = \int \left[\frac{a}{2}\phi^2 + \frac{b}{4}\phi^4 + \frac{\kappa}{2}(\nabla\phi)^2 + \frac{\gamma}{2}(\nabla^2\phi)^2 + \frac{\nu}{2}|\mathbf{p}|^2 + \lambda \mathbf{p}.\nabla\phi \right] d\mathbf{r} \tag{1}$$

Here $\mathbf{p}(\mathbf{r}) = \langle \sum_\alpha \hat{\mathbf{p}}_\alpha \delta(\mathbf{r} - \mathbf{r}_\alpha)\rangle_{\mathrm{local}}$ is a vector field where $\hat{\mathbf{p}}_\alpha$ is a unit vector pointing from tail to head of surfactant molecule α; and b, κ, γ, ν are positive constants.

(a) Interpret the scalar order parameter ϕ and state why it is a statically conserved variable in the sense that $\int \phi(\mathbf{r})\, d\mathbf{r} = V\bar{\phi} =$ constant in a system of fixed contents. Why is $\mathbf{p}$ not conserved in the same sense?

(b) Explain the physical meaning of the λ term in (1) that bilinearly couples the two fields. What determines the sign of λ?

(c) By performing the functional integral $e^{-F[\phi]} = \int e^{-F[\phi,\mathbf{p}]} D[\mathbf{p}]$, or otherwise, show that

$$F[\phi] = \int \left[\frac{a}{2}\phi^2 + \frac{b}{4}\phi^4 + \frac{\tilde{\kappa}}{2}(\nabla\phi)^2 + \frac{\gamma}{2}(\nabla^2\phi)^2 \right] d\mathbf{r}$$

and find $\tilde{\kappa}$.

[*Notes:* (i) It is not necessary to go into Fourier coordinates to perform the integral explicitly at the level of rigour required by this question. (ii) Credit can also be obtained without doing the integral explicitly, but in that case you will need to explain why the treatment you give is equivalent, for integrals of this form, to explicit integration.]

(d) What is the general effect of surfactants on interfacial tension, and why?

(e) Consider the system in the single-phase region ($a > 0$) and in one dimension (so that $\mathbf{p} = p$ and Fourier wavevectors $\mathbf{q} = q$). To study small fluctuations about a uniform (non-critical) state, we can set $b = 0$ to obtain a Gaussian model in the two variables $\Psi_i = (\phi, p)$. Show that the resulting free energy can be written

$$F[\phi, p] = \frac{1}{2} \sum_q \Psi_i(q) G_{ij}(q) \Psi_j(-q) \tag{2}$$

where $G_{ij}(q)$ is a 2×2 hermitian matrix, and give its explicit form.

(f) Show that the ϕ fluctuations obey

$$\langle \phi(q)\phi(-q)\rangle = \frac{1}{a + \tilde{\kappa} q^2 + \gamma q^4}$$

(g) Calculate also $\langle p(q)p(-q)\rangle$, and discuss the q-dependence of this correlator in relation to how the p and ϕ fluctuations are coupled via the bilinear term in (1).

2 *Answer all parts of the question.*

Consider a 2D nematic for which the local free energy density is (in the "one elastic constant" approximation)

$$\mathbb{F} = aQ_{ij}Q_{ji} + b(Q_{ij}Q_{ji})^2 + \frac{K}{2}(\nabla_i Q_{ij})(\nabla_k Q_{kj})$$

where $\mathbf{Q}$ is a traceless symmetric second-rank tensor.

(a) Show that for $a < 0$ the free energy is minimized by a uniform state with $Q_{ij} = 2\lambda_0[n_i n_j - \delta_{ij}/2]$, where $\mathbf{n}$ denotes a unit vector. Find the strength of nematic ordering, λ_0, in terms of a and b.

(b) Explain why, in a nonuniform system of slowly varying $\mathbf{Q}(\mathbf{r})$, it is a good approximation to write $Q_{ij} = 2\lambda_0[n_i(\mathbf{r})n_j(\mathbf{r}) - \delta_{ij}/2]$, ignoring any spatial variation in λ_0. Show that the resulting deformation energy is $\mathbb{F}_{\text{elastic}} = 2K\lambda_0^2|(\nabla\cdot\mathbf{n})\mathbf{n} + (\mathbf{n}\cdot\nabla)\mathbf{n}|^2$.

(c) Show that in a system where the director depends on the x coordinate only, so that $\mathbf{n} = (\cos\theta(x), \sin\theta(x)) = (c, s)$, $\mathbb{F}$ can then be written as $\mathbb{F}_{\text{elastic}} = \frac{\tilde{K}}{2}\left(\frac{d\theta}{dx}\right)^2$ and give an expression for $\tilde{K}$.

(d) Consider a 2D nematic system confined by walls at $x = 0, L$, and unbounded in y, with L large. The walls impose boundary conditions that the major axis of Q is along the x-axis at $x = 0$ but along the y-axis at $x = L$. Show that the free energy (per unit length in the y direction), $F = \int \mathbb{F}_{\text{elastic}} dx$, obeys $\delta F/\delta\theta = 0$ whenever $\theta(x) = m\pi x/2L$ with odd integer m. Show further that there are exactly two global minima, corresponding to $m = \pm 1$.

(e) Observations of one such system show that the $m = +1$ solution is approached as $y \to +\infty$ and the $m = -1$ solution is approached as $y \to -\infty$; away from these limits and the walls, θ depends on both x and y. By considering the behaviour of the director upon tracing a rectangular circuit that lies close to the walls except where $|y|$ is very large, deduce that this system must contain one or more topological defects, whose total topological charge is $q = -\frac{1}{2}$.

(f) Sketch the director field for a state of the lowest free energy consistent with these observations, and explain your reasoning as to why this state minimizes F.

(g) Suppose instead the behaviour of $\theta(x, y)$ approaches $m_+\pi x/2L$ as $y \to \infty$ and $m_-\pi x/2L$ as $y \to -\infty$, with $m_\pm$ odd integers. What is the minimum number of $|q| = \frac{1}{2}$ defects consistent with this behaviour? How many topological defects would be needed if this were instead a 3D system, with $\mathbf{r} = (x, y, z)$ unbounded in z, and $\mathbf{n}(\mathbf{r})$ a 3D unit vector subject to the same boundary conditions on $\mathbf{n}$ at $x = 0, L$, and showing the same behaviour of the director (for all z) at $y \to \pm\infty$?

3 *Answer all parts of the question.*

A particle is described by a 3D position vector $\mathbf{x}(t)$. It is governed by a classical action $A = \int \mathcal{L}(\mathbf{x}, \dot{\mathbf{x}})\, dt$ with time independent Lagrangian, and coupled to an equilibrium heat bath that creates a drag force $-\zeta\dot{\mathbf{x}}$ and a thermal white-noise force $\mathbf{f}$. That is,

$$-\frac{\delta A}{\delta \mathbf{x}(t)} = -\zeta\dot{\mathbf{x}} + \mathbf{f} \tag{1}$$

where the probability density of the noise is $\mathbb{P}[\mathbf{f}(t)] = \mathcal{N} \exp\left[-\frac{1}{2\sigma^2}\int |\mathbf{f}(t)|^2\, dt\right]$.

(a) Give an expression for the probability density $\mathbb{P}_F[\mathbf{x}(t)]$ of a trajectory starting at $(\mathbf{x}_1, t_1)$ and ending at $(\mathbf{x}_2, t_2)$. Give also the probability density $\mathbb{P}_B[\mathbf{x}(t)]$ of a time-reversed trajectory, where time reversal means $\dot{\mathbf{x}} \to -\dot{\mathbf{x}}$ but no sign change for $-\frac{\delta A}{\delta \mathbf{x}(t)}$ in (1). Stating any assumptions that you need to make, show that

$$\frac{\mathbb{P}_F[\mathbf{x}(t)]}{\mathbb{P}_B[\mathbf{x}(t)]} = \exp\left[\frac{2\zeta}{\sigma^2}\int_1^2 \dot{\mathbf{x}} \cdot \frac{\delta A}{\delta \mathbf{x}(t)}\, dt\right] \tag{2}$$

where the limits $1, 2$ on the integral denote initial and final states.

(b) Show that the integrand in (2) is $-dH/dt$, where $H(\mathbf{x}, \dot{\mathbf{x}}) \equiv \dot{\mathbf{x}}\cdot\partial\mathcal{L}/\partial\dot{\mathbf{x}} - \mathcal{L}$ is Hamilton's function.

(c) Briefly explain the principle of detailed balance, and say why it requires $\mathbb{P}_F/\mathbb{P}_B = \exp[-\beta\Delta H]$, where the notation should be explained. Find σ^2 in terms of β and ζ.

(d) Consider now a particle obeying (1) but with an additional term $\mathbf{F}$ added to the right hand side, representing an external force acting on the particle. Show that in this case

$$\frac{\mathbb{P}_F[\mathbf{x}(t)]}{\mathbb{P}_B[\mathbf{x}(t)]} = \exp\left[-\beta\Delta H + \beta\int_1^2 \mathbf{F}(\mathbf{x}) \cdot \dot{\mathbf{x}}\, dt\right] \tag{3}$$

(e) Identifying the integral in (3) as the work done by $\mathbf{F}$, show that

$$\frac{\mathbb{P}_F[\mathbf{x}(t)]}{\mathbb{P}_B[\mathbf{x}(t)]} = \exp[\beta\Delta Q] \tag{4}$$

where ΔQ is the energy lost as heat to the thermal bath. (You may assume that in the first law of thermodynamics the internal energy E is numerically equal to H.)

(f) Assuming that H, $\mathbf{F}$, and $|\mathbf{x}|$ all remain bounded, show that ΔQ can increase linearly with $\Delta t = t_2 - t_1$, even as this time interval becomes very large, only if $\operatorname{curl}\mathbf{F} \neq \mathbf{0}$.

(g) A thermal system with nonconserved vector order parameter $\mathbf{p}(\mathbf{r})$ and free energy $F[\mathbf{p}]$ obeys

$$\dot{\mathbf{p}}(\mathbf{r}) = \Gamma\left(-\frac{\delta F}{\delta \mathbf{p}(\mathbf{r})} + \mathbf{Y}\right) + \sqrt{2k_BT\Gamma}\,\boldsymbol{\Lambda}(\mathbf{r}, t)$$

where $\mathbb{P}[\boldsymbol{\Lambda}] \propto \exp[-\frac{1}{2}\int |\boldsymbol{\Lambda}(\mathbf{r}, \mathbf{t})|^2\, d\mathbf{r}\, dt]$, and the usual molecular field term is augmented by an extra term $\mathbf{Y}(\mathbf{r}, [\mathbf{p}])$ to represent an external forcing. Derive and interpret the result

$$\frac{\mathbb{P}_F[\mathbf{p}(\mathbf{r}, t)]}{\mathbb{P}_B[\mathbf{p}(\mathbf{r}, t)]} = \exp\left[-\beta\Delta F + \beta\int_1^2 (\mathbf{Y} \cdot \dot{\mathbf{p}})\, d\mathbf{r}\, dt\right].$$

END OF PAPER