UNIVERSITY OF CAMBRIDGE

MAT3, MAMA, NST3AS

MATHEMATICAL TRIPOS Part III

Monday, 10 June, 2019 1:30 pm to 3:30 pm

PAPER 344

THEORETICAL PHYSICS OF SOFT CONDENSED MATTER

*Full marks can be achieved by complete answers to **TWO** questions.*

If you hand in more than two answers, all will be marked but the lowest mark is liable to be discounted.

*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.*

Assume $\beta \equiv 1/k_BT = 1$ throughout this question.

The composition $\phi(\mathbf{r})$ in a certain system obeys $\int \phi \, d\mathbf{r} = 0$ and, is governed by a free energy functional

$$H = \int \left(\frac{a}{2}\phi^2 + \frac{\kappa}{2}(\nabla\phi)^2 + \frac{\gamma}{2}(\nabla^2\phi)^2 + B(\nabla\phi)^2\phi^2 \right) d\mathbf{r} \,. \tag{1}$$

(a) Show that, for negative κ and $B = 0$, upon reducing a the system becomes unstable to smectic ordering at wavenumber $q_0 = (-\kappa/2\gamma)^{1/2}$.

(b) Assuming a functional form $\phi(\mathbf{r}) = A\cos(q_0 z)$, where z is an arbitrary direction, find for nonzero B the resulting mean-field free energy per unit volume as a function of the smectic amplitude A, and show that at this level a continuous transition is predicted at some $a = a_c$ which you should find.

(c) Starting from the identity

$$e^{-F} = e^{-F_0}\langle e^{-(H-H_0)}\rangle_0,$$

explain the basis of the Feynman-Bogoliubov inequality $F \leqslant F_0 - \langle H_0\rangle_0 + \langle H\rangle_0$, where $\langle X\rangle_0$ denotes $Z_0^{-1}\int X e^{-H_0} D[\phi]$.

(d) In Fourier variables $\phi_{\mathbf{q}}$, Eq.(1) can be written

$$H = \sum_{\mathbf{q}}^{+} G(q)\phi_{\mathbf{q}}\phi_{-\mathbf{q}} + \frac{B}{V}\sum_{\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3} (-\mathbf{q}_1\cdot\mathbf{q}_2)\,\phi_{\mathbf{q}_1}\phi_{\mathbf{q}_2}\phi_{\mathbf{q}_3}\phi_{-\mathbf{q}_1-\mathbf{q}_2-\mathbf{q}_3} \tag{2}$$

where $\sum^{+}$ denotes a sum over the half space $q_x > 0$ (say), and $G(q) = a + \kappa q^2 + \gamma q^4$. (You are not asked to prove Eq.(2).)

Choosing as trial functional $H_0 = \sum_{\mathbf{q}}^{+} J(q)\phi_{\mathbf{q}}\phi_{-\mathbf{q}}$, for which $F_0 = \sum_{\mathbf{q}}^{+}\ln(J(q)/\pi)$ and $\langle H_0\rangle_0 = \sum_{\mathbf{q}}^{+} 1$, use the property of zero-mean Gaussian random variables $\langle X_1X_2X_3X_4\rangle = \langle X_1X_2\rangle\langle X_3X_4\rangle + \langle X_1X_3\rangle\langle X_2X_4\rangle + \langle X_1X_4\rangle\langle X_2X_3\rangle$ to establish that

$$F \leqslant \sum_{\mathbf{k}}^{+}\left(\ln(J(k)/\pi) - 1 + \frac{G(k)}{J(k)}\right) + \frac{4B}{V}\left[\sum_{\mathbf{k}}^{+}\frac{k^2}{J(k)}\right]\left[\sum_{\mathbf{k}}^{+}\frac{1}{J(k)}\right],$$

after excluding contributions that are negligible for V large and/or vanish by symmetry.

(e) By minimizing over $J(q)$, and then taking the large V limit so that $\sum_{\mathbf{k}}^{+} X(k) \to \frac{V}{2(2\pi)^d}\int X(k)d\mathbf{k}$, show that the least upper bound on F arises for the variational choice

$$J(q) = \bar{a} + \bar{\kappa}q^2 + \gamma q^4 \tag{3}$$

and give a pair of coupled integral equations satisfied by $\bar{a}$ and $\bar{\kappa}$.

(f) Give a brief reasoned argument for whether the transition to the smectic phase should be continuous or discontinuous in this model.

2 *Answer all parts of the question.*

A system is described by a coarse-grained vector order parameter field $\mathbf{p}(\mathbf{r}, t)$ which obeys the Langevin equation

$$\dot{\mathbf{p}}(\mathbf{r}, t) = -\Gamma \frac{\delta F}{\delta \mathbf{p}(\mathbf{r}, t)} + \mathbf{f}(\mathbf{r}, t)$$

where $F[\mathbf{p}(\mathbf{r})]$ is the free energy, Γ a constant coefficient and $\mathbf{f}$ is Gaussian white noise of probability density $\mathbb{P}[\mathbf{f}(\mathbf{r}, t)] = \mathcal{N} \exp\left[-\frac{1}{2\sigma^2} \int |\mathbf{f}(\mathbf{r}, t)|^2 \, d\mathbf{r} \, dt\right]$ with $\mathcal{N}$ a normalization constant. The noise is caused by coupling to a heat bath at temperature T.

(a) State the probability density $\mathbb{P}_F[\mathbf{p}(\mathbf{r}, t)]$ for a time evolution $\mathbf{p}(\mathbf{r}, t)$ connecting an initial configuration $\mathbf{p}_1(\mathbf{r}, t_1)$ of free energy F_1, to a final configuration $\mathbf{p}_2(\mathbf{r}, t_2)$ of free energy F_2. Write down $\mathbb{P}_B[\mathbf{p}(\mathbf{r}, t)]$, the probability density for the time-reversed trajectory, and briefly explain why the two expressions have the same normalization factor.

(b) Show that

$$\frac{\mathbb{P}_F}{\mathbb{P}_B} = \exp\left[-\frac{2\Gamma}{\sigma^2} \int_1^2 \dot{\mathbf{p}} \frac{\delta F}{\delta \mathbf{p}} \, d\mathbf{r} \, dt\right],$$

and explain why, if the underlying microscopic dynamics has time-reversal symmetry, this implies that $\sigma^2 = 2\Gamma k_B T$.

(c) Consider the case where $\delta F/\delta \mathbf{p} = a\mathbf{p} - \kappa \nabla^2 \mathbf{p}$ with $a, \kappa > 0$. Suppose the system was put in contact with the heat bath in the remote past ($t = -\infty$) and undisturbed since then. Establish that in Fourier variables $\mathbf{p_q}(t)$, $\mathbf{p_q}(t) = \int_{-\infty}^{t} \mathbf{f_q}(t') \exp[-r(q)(t - t')] \, dt'$, and give an expression for $r(q)$. Hence or otherwise show that the spatiotemporal correlations of the order parameter obey

$$\langle p_{\mathbf{q},i}(t_1) p_{-\mathbf{q},j}(t_2) \rangle = \delta_{ij} \frac{k_B T}{a + \kappa q^2} \exp[-r(q)|t_1 - t_2|]$$

where $p_{\mathbf{q},i}$ is the ith Cartesian component of the vector $\mathbf{p_q}$. You may assume without proof that $\langle f_{\mathbf{q},i}(t) f_{-\mathbf{q},j}(t') \rangle = 2k_B T \Gamma \delta_{ij} \delta(t - t')$.

(d) The system's dynamics is now changed, allowing the order parameter to relax by two independent channels, one corresponding to nonconserved dynamics and the other conserved. The equations of motion are

$$\begin{aligned} \dot{p}_j(\mathbf{r}, t) &= -\nabla_i W_{ij} - \Gamma \frac{\delta F}{\delta p_j(\mathbf{r}, t)} + f_j(\mathbf{r}, t), \\ W_{ij}(\mathbf{r}, t) &= -M \nabla_i \frac{\delta F}{\delta p_j(\mathbf{r}, t)} + N_{ij}(\mathbf{r}, t). \end{aligned}$$

Here W_{ij} is the flux along i of p_j and, alongside f_j as defined above, N_{ij} is a Gaussian white noise obeying $\mathbb{P}[N_{ij}(\mathbf{r}, t)] = \mathcal{N}_N \exp\left[-\frac{1}{2\sigma_N^2} \int N_{ij}(\mathbf{r}, t) N_{ij}(\mathbf{r}, t) \, d\mathbf{r} \, dt\right]$. Construct the forward and backward path probabilities $\mathbb{P}_{F,B}[\mathbf{p}(\mathbf{r}, t), \mathbf{W}(\mathbf{r}, t)]$ for the joint time evolution of $\mathbf{p}$ and $\mathbf{W}$, and give an expression for their ratio. It may help to note that, by the usual law of conditional probabilities, $\mathbb{P}[\mathbf{p}, \mathbf{W}] = \mathbb{P}[\mathbf{p}|\mathbf{W}] \mathbb{P}[\mathbf{W}]$.

(e) Assuming that $\mathbf{p}$ and $\mathbf{W}$ both obey periodic boundary conditions in space, show that microscopic reversibility remains satisfied if both $\sigma^2 = 2\Gamma k_B T$ and $\sigma_N^2 = 2M k_B T$.

3 *Answer all parts of the question.*

A system has conserved scalar order parameter $\phi(\mathbf{r})$ and a free energy $F = \int \mathbb{F}\, d\mathbf{r}$ where $\mathbb{F} = f(\phi) + \frac{\kappa}{2}(\nabla\phi)^2$ and $f(\phi) = \frac{a}{2}\phi^2 + \frac{b}{4}\phi^4$.

(a) Show by minimizing F that at mean-field level, for negative a, bulk phases coexist with $\pm\phi_B$ where $\phi_B = (-a/b)^{1/2}$. Show that the same result can be viewed as requiring equality between phases of the bulk chemical potential $\mu = f'(\phi)$ and bulk pressure $\Pi = \mu\phi - f$.

(b) Consider a 3D droplet geometry, with droplet radius R large compared to the interfacial width ξ_0. Show by force balance that the bulk pressures inside and outside the droplet must differ by a Laplace pressure term $2\gamma/R$ where γ is the interfacial tension. [You are *not* asked to calculate ξ_0 or γ in terms of a, b, κ]. Show that this leads to a modified coexistence condition $\phi = \pm\phi_B + \delta$ where $\delta = \frac{\gamma}{\alpha\phi_B R}$ with $\alpha = f''(\pm\phi_B)$. Why are the chemical potentials still equal?

(c) Consider now a 3D droplet of $\phi = \phi_B + \delta$ residing within a bulk phase that has $\phi = -\phi_B$ at infinity. Supposing the coexistence condition from (b) to still apply locally, and considering a quasi-static exterior solution $\nabla^2\mu = 0$ of the diffusion equation $\dot{\phi} = -\nabla.\mathbf{J}$, calculate the current $\mathbf{J} = -M\nabla\mu$ leaving the droplet surface and use this to find the time derivative of the radius R. Exterior to the droplet you may neglect gradient contributions to the local chemical potential $\mu = \delta F/\delta\phi$ and linearise its ϕ dependence.

(d) Show that the droplet evaporates entirely in a time $\tau(R_0) = 2\phi_B^2 R_0^3/(3M\gamma)$ where R_0 is its initial radius.

(e) Suppose now that a similar droplet of radius R has its centre maintained at a fixed distance h (with $h - R \gg \xi_0$) from a flat interface beyond which lies an infinite bulk of the $\phi = \phi_B$ phase. Again consider a quasi-static solution and neglect higher gradient terms in μ; furthermore, assume that the droplet remains spherical as it shrinks. By establishing an analogy between $\nabla^2\mu = 0$ with the appropriate boundary conditions and an electrostatics problem, or otherwise, show that the total current $\int \mathbf{J}.d\mathbf{S}$ leaving the droplet surface is modified from that in part (c) above by a factor $c(R/h) \equiv C(R,h)/C(R,\infty)$ where $C(R,h)$ is the electrostatic capacitance of a conducting sphere of radius R whose centre is at a distance h from an infinite plane conductor.

(f) A closed-form approximation to the function $c(y)$ can be found in the electrostatics literature as

$$c(y) \simeq 1 + \frac{1}{2}\ln(1+y) \ .$$

Within this approximation, calculate the leading order correction in small R_0/h to the evaporation time $\tau(R_0)$ as defined in part (d).

END OF PAPER