THE UNIVERSITY OF WARWICK

FOURTH YEAR EXAMINATION: APRIL 2007

INTRODUCTION TO STATISTICAL MECHANICS

Time Allowed: **3 hours**

Read carefully the instructions on the answer book and make sure that the particulars required are entered on each answer book.

Calculators are not needed and are not permitted in this examination.

ANSWER 4 QUESTIONS.
If you have answered more than the required 4 questions in this examination, you will only be given credit for your 4 best answers.

The numbers in the margin indicate approximately how many marks are available for each part of a question.

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1. (Thermodynamic potential of the ideal gas)

a) Give the definition of the Boltzmann entropy of a (classical) gas of particles with two-body interactions. **[5]**

b) Show that the pressure of the *ideal* gas (i.e. without interactions) is $p(\beta, \mu) = (\frac{2\pi}{\beta})^{d/2}\,\mathrm{e}^{\beta\mu}$. Here, β denotes the inverse temperature, μ the chemical potential, and d the dimension (physical constants such as the mass of particles or Planck's constant were set to 1). **[10]**

c) Use the equivalence of ensembles to get the free energy $f(\beta, n)$ of the ideal gas, where n is the density. **[10]**

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2. Consider the antiferromagnetic Ising model in one dimension. Let $w = (w_1, \dots, w_N)$ denote a configuration of spins $w_i = \pm 1$. The Hamiltonian is

$$H(w) = \sum_{i=1}^{N} w_i w_{i+1}$$

with $w_{N+1} = w_1$ (periodic boundary conditions). Recall that the free energy is defined by

$$q_N(\beta, h) = -\frac{1}{\beta N} \log \sum_w \mathrm{e}^{-\beta[H(w) - hM(w)]},$$

where $M(w) = \sum_{i=1}^{N} w_i$.

a) Find 2×2 transfer matrices $T = T(\beta, h)$ such that

$$\sum_w \mathrm{e}^{-\beta[H(w) - hM(w)]} = \operatorname{Tr} T^N.$$

[15]

b) Find $\lim_{N\to\infty} q_N(\beta, h)$. (If you did not get the transfer matrix in (a), explain how the method works.) **[10]**

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3. a) (Laplace principle). Let $f : [a,b] \to \mathbb{R}$ be continuous. Prove that

$$\lim_{N\to\infty} \frac{1}{N} \log \int_a^b \mathrm{e}^{Nf(x)}\, \mathrm{d}x = \max_{a \leqslant x \leqslant b} f(x).$$

[10]

b) Consider the (ferromagnetic) Ising model with state space $\Omega = \{-1,1\}^D$, where $D \subset \mathbb{Z}^d$ is finite, and with Hamiltonian

$$H(w) = -\sum_{\substack{\{x,y\}\subset D \\ |x-y|=1}} w(x)w(y).$$

Recall that

$$q_D(\beta,h) = -\frac{1}{\beta|D|} \log \sum_{w\in\Omega} \mathrm{e}^{-\beta[H(w)-hM(w)]},$$

with $M(w) = \sum_{x\in D} w(x)$. Prove that

$$\lim_{\beta\to\infty} q_D(\beta,h) = \min_{w\in\Omega} \frac{1}{|D|}\big[H(w) - hM(w)\big].$$

[10]

c) Compute explicitly $\lim_{\beta\to\infty} q_D(\beta,h)$, where D is a d-dimensional cube with periodic boundary conditions. **[5]**

4. Consider the classical gas of particles in the continuum, in d dimensions. Particles at distance $q \in \mathbb{R}^d$ interact with the two-body potential

$$U(q) = \begin{cases} \infty & \text{if } |q| < 1 \\ -|q|^{-\eta} & \text{if } |q| \geqslant 1. \end{cases}$$

Here, $\eta > 0$ is a fixed parameter. Recall that a potential is *stable* if there exists a constant B such that for any $N \in \mathbb{N}$, and any $q_1, \dots, q_N \in \mathbb{R}^d$,

$$\sum_{1 \leqslant i<j \leqslant N} U(q_i - q_j) > -BN.$$

a) Prove that the potential is *not* stable if η is sufficiently small. (Hint: Do it in one dimension, $d = 1$, and observe that the result holds for arbitrary d.) **[10]**

b) Prove that the potential is stable when $d = 1$, and η is sufficiently large. **[10]**

c) What is the limiting value for η, in arbitrary dimensions? No need to prove the answer, but give a convincing argument. **[5]**

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5. (Essay about phase transitions)

a) Give a brief description of the phenomenon of phase transitions. [**5**]

b) Describe the relation between phase transitions and the mathematical properties of thermodynamic potentials. [**10**]

c) Describe rigorous results about the Ising model, and their relations with the question of phase transitions. [**10**]

MA4G3

In order for the external checker to have an idea of what topics were covered in the class, I include the class notes that were handled to the students.

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Model Solution No: 1

a) The Hamiltonian for the classical gas is

$$H(\{p_i\},\{q_i\}) = \sum_{\imath=1}^{N} p_i^2 + \sum_{1\leqslant i<j\leqslant N} V(q_i - q_j),$$

where $p_1, \dots, p_N$ and $q_1, \dots, q_N$ are the momenta and the positions of the N particles. With $D \subset \mathbb{R}^d$ a bounded set denoting the domain of the system, Boltzmann entropy is

$$S(U, D, N) = \log \int_{\mathbb{R}^{dN}} \mathrm{d}p_1 \dots \mathrm{d}p_N \int_{D^N} \mathrm{d}q_1 \dots \mathrm{d}q_N \, \mathbb{1}_{[H(\{p_i\},\{q_i\})<U]}.$$

Here, U denotes the energy, and $\mathbb{1}_{[\cdot]}$ is the indicator function.
b) This problem is new to students. For the ideal gas, we have

$$\begin{aligned} p(\beta,\mu) &= \lim_{D\nearrow\mathbb{Z}^d} \frac{1}{|D|} \log \sum_{N\geqslant 0} \frac{\mathrm{e}^{\beta\mu N}}{N!} \int_{\mathbb{R}^{dN}} \mathrm{d}p_1 \dots \mathrm{d}p_N \int_{D^N} \mathrm{d}q_1 \dots \mathrm{d}q_N \, \mathrm{e}^{-\beta \sum_{i=1}^N p_i^2} \\ &= \lim_{D\nearrow\mathbb{Z}^d} \frac{1}{|D|} \log \Big[\sum_{N\geqslant 0} \frac{\mathrm{e}^{\beta\mu N}}{N!} |D|^N \Big(\int_{\mathbb{R}^d} \mathrm{e}^{-\beta p_i^2} \, \mathrm{d}p_i \Big)^N \Big] \\ &= \Big(\frac{2\pi}{\beta}\Big)^{d/2} \mathrm{e}^{\beta\mu}. \end{aligned}$$

c) The free energy is given by a Legendre transform of the pressure, and the pressure has just been computed. With n the density, we have

$$f(\beta, n) = \sup_\mu [\mu n - p(\beta,\mu)] = \sup_\mu \big[\mu n - (\tfrac{2\pi}{\beta})^{d/2} \mathrm{e}^{\beta\mu}\big].$$

The maximum of the bracket occurs when

$$0 = \tfrac{\partial}{\partial\mu} \big[\mu n - (\tfrac{2\pi}{\beta})^{d/2} \mathrm{e}^{\beta\mu}\big] = n - \beta (\tfrac{2\pi}{\beta})^{d/2} \mathrm{e}^{\beta\mu}.$$

Then $\mathrm{e}^{\beta\mu} = \frac{n}{\beta} (\frac{\beta}{2\pi})^{d/2}$, and

$$f(\beta, n) = \tfrac{n}{\beta} \log \big[\tfrac{n}{\beta} (\tfrac{\beta}{2\pi})^{d/2}\big] - \tfrac{n}{\beta}.$$

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Model Solution No: 2

a) We did the computation for the ferromagnetic model, so this exercise was essentially done in class. We have

$$\sum_w \mathrm{e}^{-\beta[\sum_i w_i w_{i+1} - h \sum_i w_i]} = \sum_w \prod_{i=1}^N \underbrace{\mathrm{e}^{-\beta w_i w_{i+1} + \frac{1}{2}\beta h (w_i + w_{i+1})}}_{T_{w_i, w_{i+1}}} = \operatorname{Tr} T^N,$$

where

$$T = \begin{pmatrix} \mathrm{e}^{-\beta+\beta h} & \mathrm{e}^{\beta} \\ \mathrm{e}^{\beta} & \mathrm{e}^{-\beta-\beta h} \end{pmatrix}.$$

b) Eigenvalues of T are easily computed; we get

$$\lambda_\pm = \mathrm{e}^{-\beta} \cosh \beta h \pm \sqrt{\mathrm{e}^{-2\beta} \cosh^2 \beta h + 2 \sinh 2\beta}.$$

The largest eigenvalue is λ_+. Then

$$\operatorname{Tr} T^N = \lambda_+^N + \lambda_-^N,$$

and

$$\lim_{N\to\infty} \frac{1}{N} \log \operatorname{Tr} T^N = \log \lambda_+.$$

The answer is therefore

$$\lim_{N\to\infty} q_N(\beta, h) = -\frac{1}{\beta} \log\Big[\mathrm{e}^{-\beta} \cosh \beta h + \sqrt{\mathrm{e}^{-2\beta} \cosh^2 \beta h + 2 \sinh 2\beta} \Big].$$

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Model Solution No: 3

a) This problem was essentially in the assignments. Since $f(x) \leqslant \max_y f(y)$, it is clear that

$$\lim \frac{1}{N} \log \int_a^b \mathrm{e}^{Nf(x)} \,\mathrm{d}x \leqslant \max f(x).$$

But since f is continuous, for any $\varepsilon > 0$ there exists an open interval (c, d) such that

$$f(y) > \max f(x) - \varepsilon,$$

for any $y \in (c, d)$. Then

$$\begin{aligned} \frac{1}{N} \log \int_a^b \mathrm{e}^{Nf(x)} \,\mathrm{d}x &\geqslant \frac{1}{N} \log\Big[(d-c)\,\mathrm{e}^{N \max f(x)}\ \mathrm{e}^{-N\varepsilon}\Big] \\ &= \frac{1}{N} \log(d-c) + \max f(x) - \varepsilon. \end{aligned}$$

Taking first the limit $N \to \infty$ then the limit $\varepsilon \to 0$, one gets the result.
b) This was not discussed in the course, but the situation is similar to Laplace principle. Let w_0 be a minimizer for $H(w) - hM(w)$. Then

$$-\frac{1}{\beta|D|} \log \sum_{w \in \Omega} \mathrm{e}^{-\beta[H(w) - hM(w)]} \geqslant \frac{1}{|D|}[H(w_0) - hM(w_0)].$$

Since $|\Omega| = 2^{|D|}$, we also have

$$\begin{aligned} -\frac{1}{\beta|D|} \log \sum_{w \in \Omega} \mathrm{e}^{-\beta[H(w) - hM(w)]} &\leqslant -\frac{1}{\beta|D|} \log\Big[2^{|D|}\,\mathrm{e}^{-\beta[H(w_0) - hM(w_0)]}\Big] \\ &= -\frac{1}{\beta} \log 2 + \frac{1}{|D|}\big[H(w_0) - hM(w_0)\big]. \end{aligned}$$

As $\beta \to \infty$, the first term of the right side vanishes.
c) The minimizers for $H(w) - hM(w)$ are either $w_0(x) \equiv 1$ (if $h \geqslant 0$), or $w_0(x) \equiv -1$ (if $h \leqslant 0$). Either way, we have that $H(w_0)$ is equal to the negative of the number of nearest neighbours in D, i.e. $-d|D|$. And $M(w_0) = -|h||D|$. Then

$$\lim_{\beta \to \infty} q_D(\beta, h) = -d - |h|.$$

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Model Solution No: 4

There was a similar exercise in the assignments.
a) Consider N particles along a line, separated by distance 1. Then

$$\sum_{1 \leqslant i<j \leqslant N} U(q_i - q_j) = -\sum_{\ell=1}^{N-1} \ell^{-\eta} \#\big\{(i,j) : i<j \text{ and } |q_i - q_j| = \ell\big\}$$
$$\leqslant -\tfrac{1}{2} N \sum_{\ell=1}^{N/2} \ell^{-\eta} \leqslant -\operatorname{const} N \log N$$

if $\eta \leqslant 1$. There exists therefore no constant B such that the left side is larger than $-BN$ for any N.
b) Since $U(q_i - q_j) = \infty$ if $|q_i - q_j| < 1$, we need to establish the lower bound for $q_1 < q_2 < \cdots < q_N$ such that $q_{i+1} - q_i \geqslant 1$ for all i. We have $|q_i - q_j| \geqslant |i-j|$, and therefore

$$\sum_{1 \leqslant i<j \leqslant N} U(q_i - q_j) = -\sum_{1 \leqslant i<j \leqslant N} |q_i - q_j|^{-\eta} \geqslant -\sum_{1 \leqslant i<j \leqslant N} |i-j|^{-\eta}$$
$$\geqslant -\sum_{i=1}^{N-1} \underbrace{\sum_{j=1}^{N-i} j^{-\eta}}_{\leqslant \operatorname{const} \forall N} \geqslant -\operatorname{const} N.$$

c) The lowest value for $\sum U(q_i - q_j)$ corresponds to a configuration of packed spheres of radius 1. Upper and lower bounds for the potential energy felt by one particle are

$$\sum_{\ell=1}^{\infty} \ell^{-\eta} \#\big\{j : \ell \leqslant |q_i - q_j| < \ell+1\big\},$$
$$\sum_{\ell=1}^{\infty} (\ell+1)^{-\eta} \#\big\{j : \ell \leqslant |q_i - q_j| < \ell+1\big\}.$$

For large ℓ, the number of elements in the set is roughly proportional to the volume of the shell with outer radius $\ell+1$ and inner radius ℓ. Precisely, there exist constants c_1, c_2 such that

$$c_1 \ell^{d-1} \leqslant \#\big\{j : \ell \leqslant |q_i - q_j| < \ell+1\big\} \leqslant c_2 \ell^{d-1}.$$

Then the question boils down to whether $\sum_\ell \ell^{d-1-\eta}$ is finite or infinite, and so the limiting value is $\eta = d$.

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Model Solution No: 5

To answer this question, the student needs an overall understanding of the topic of the course.
a) Phase transitions are cooperative phenomena, where a dramatic change of the behaviour of the system occurs when the environment is slightly modified. An example is the transition from solid to liquid, or from liquid to gas.
b) Thermodynamic potentials are not analytic at points with a phase transition. In first order phase transitions, such as liquid-solid, we have that

- the entropy is locally flat;
- the free energy is flat with respect to the density, or it has a cusp with respect to the temperature;
- the pressure has cusps.

c) We have computed the free energy of the one-dimensional Ising model. It is analytic in β, h, and no phase transitions occurs. By contrast, we used the Peierls argument to prove that, in two dimensions and for β large enough (i.e. sufficiently low temperature), the free energy $f(\beta, h)$ has a cusp at $h = 0$:

$$D_{-h} f(\beta, h)\big|_{h=0} > 0 > D_{+h} f(\beta, h)\big|_{h=0}.$$