# INTERNATIONAL SCHOOL FOR ADVANCED STUDIES
## 1996 ENTRANCE EXAMINATION: CONDENSED MATTER

Solve at least one of the problems below (the order is irrelevant). Write out solution clearly and concisely. State each approximation used. Diagrams welcome. Number pages, problem, and question clearly. Do not write your name on the problems sheet, but use extra envelope. A single well-solved problem is better than many half-solved ones.

## Problem 1
## Two bosons or fermions on a large circle

Two particles, with statistics to be specified, equal mass $m$ and coordinates $x_1, x_2$ are confined to move on a one-dimensional line of large but finite lenght $L$. The one-dimensional motion is free, but the two particles interact with each other through a potential $V(x_1 - x_2) = V_0\delta(x_1 - x_2)$. Assume the boundary conditions to be periodic, so that the line can be seen as a large circle. With an accuracy on the energy sufficiently good to include terms of order $1/L^2$, but neglecting all higher corrections, find the solution to Schroedinger's equation for the ground state energy $E_0$ and wave function $\psi_0(x_1, x_2)$, respectively for
1) Two (spinless) fermions, for any sign of $V_0$.
2) Two bosons, for large attractive interaction ($V_0 << 0$) [Hint: consider only the case where $L$ is really large!].
3) Two bosons, for infinitely large repulsive interaction ($V_0 \rightarrow \infty$). Compare the result with the fermionic case.
4) Calculate the "coincidence probability" $|\psi_0(x_1 = x_2)|^2$, for all cases above, and where pertinent discuss its dependence on $V_0$.

## Problem 2
## Self-diffusion in the hydrodynamic limit

Consider a group of particles (within a classical fluid) which at time $t = 0$ are found in a small volume around $\mathbf{r} = 0$. At time $t$ the fraction of these particles at point $\mathbf{r}$ is $G_s(\mathbf{r}, t)$. In the hydrodynamic limit $G_s(\mathbf{r}, t)$ obeys Fick's diffusion law:

$$\frac{d}{dt} G_s(\mathbf{r}, t) = D \, \nabla^2 G_s(\mathbf{r}, t) \tag{1}$$

1

where D is the diffusion coefficient.

1. solve this equation under the initial condition $G_s(\mathbf{r}, t) = \delta(\mathbf{r}, 0)$ and assuming the system to be an isotropic liquid. [Hint: use the trial function $e^{-\frac{r^2}{\gamma(t)}}$, where $\gamma(t)$ is a generic function of time, properly normalized to the initial condition].

2. show that if (1) holds the diffusion coefficient is given by the well known Einstein relation:

$$D = \lim_{t \to \infty} \frac{1}{6t} \langle \, |\mathbf{r}(t) - \mathbf{r}(0)|^2 \, \rangle \tag{2}$$

3. starting from this expression show that D can also be espressed in the form

$$D = \frac{1}{3} \int_0^\infty \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle \, dt \tag{3}$$

4. For a simple liquid (such as, e.g., argon near the triple point) sketch the behaviour as a function of time of the correlation functions $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$ and $\langle \, |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$, discussing in particular the small time and large time limits.

5. (optional) indicate the order of magnitude of D in simple liquids (e.g. argon near the triple point).

**Problem 3**
**A linear chain of particles**

A chain of $N$ classical particles at positions $\vec{r}_i \in \Re^d$, $1 \le i \le N$, is in thermal equilibrium at temperature $T$ (assume $K_B = 1$). If the Hamiltonian of the system is:

$$\mathcal{H} = \sum_{i=1}^{N-1} V(\vec{r}_i - \vec{r}_{i+1}) \tag{1}$$

(the kinetic energy is omitted) calculate:

1. the partition function

$$\mathcal{Z}_0 = \int \mathrm{d}^d\vec{r}_2 \dots \mathrm{d}^d\vec{r}_N \ e^{-\mathcal{H}/T} \qquad (2)$$

where particle 1 is pinned at the origin, $\vec{r}_1 \equiv O$, (and

$$I \equiv \int \mathrm{d}^d\vec{r}\, e^{-V(\vec{r})/T} \qquad (3)$$

is assumed to be known),

2. the partition function $\mathcal{Z}(\vec{f})$ when a constant force, $\vec{f}$, is applied to the $N$-th particle.

[*Hint:* add $-\vec{f} \cdot \vec{r}_N$ to the Hamiltonian and use

$$\vec{r}_N = -\sum_{i=1}^{N-1} \vec{r}_i - \vec{r}_{i+1}, \qquad \qquad ]$$

3. the explicit formula for the average displacement of $\vec{r}_N$ and its variance in presence of $\vec{f}$ if $V(\vec{r}) = \frac{k}{2}|r|^2$.

[*Hint:* use

$$\int \mathrm{d}^d\vec{r}\, e^{-a|r|^2 + \vec{b} \cdot \vec{r}} = (\frac{\pi}{a})^{d/2}\, e^{\frac{b^2}{4a}}, \qquad \qquad ]$$

4. the probability, $P(\vec{R}) \equiv \langle \delta(\vec{r}_N - \vec{R}) \rangle$ of the extremum $\vec{r}_N$ to be in $\vec{R}$ when the force $\vec{f}$ is present (use the Fourier transform of a Dirac's $\delta$ function).

## Problem 4
## Ground State Geometry of a Trimer

A molecule consisting of three identical atoms may exist in two alternative forms: either as an equilateral triangle or a as a linear chain. Electrons may be considered non-interacting and the single-particle wavefunctions are linear combinations of atomic orbitals: a single $s$-state is centered on each atom, and states on different atoms are assumed orthogonal. The bond lengths

3

are constant and the single-particle hamiltonian matrix elements are all zero except those between nearest neighbour atoms which are all $-|\beta|$.

*a)* Discuss the symmetry properties of the molecule in the two configurations.

*b)* Determine the molecular configuration with the lowest electronic energy as a function of the total number of electrons in the molecule from one to six. Discuss the electronic degeneracy of the ground state in each case.

Release the hypothesis of rigid molecule and assume for the triangular case that deviation from equilateral geometry imply simultaneously a change in the nearest-neighbour interaction and an elastic energy cost:

$$\beta_i = \beta + \beta' \left( \frac{2\pi}{3} - \alpha_i \right), \qquad E_{elast} = \frac{1}{2} K \sum_{i=1}^{3} \left( \frac{2\pi}{3} - \alpha_i \right)^2$$

where $\alpha_i$ is the internal angle opposite the $i$-th bond.

*c)* Determine the new ground state configuration and ground state energy as a function of the total number of electrons in the molecule from one to three. Discuss the degeneracy of the ground state.

## Problem 5
## Electron wavefunction in a non local external field

An electron is localized in a harmonic potential, centered around the position $x = a$: $V(x) = \frac{1}{2}(x - a)^2$. Suppose also that the electron is subject to a non local external field that opens an energy gap $\Delta$ between the even $\psi(x) = \psi(-x)$ and the odd $\psi(x) = -\psi(-x)$ components of the electron wavefunction $\psi(x)$. The Schrödinger equation then reads:

$$-\frac{\hbar^2}{2m} \partial_x^2 \psi(x) + V(x)\psi(x) - \frac{\Delta}{2}\psi(-x) = E\psi(x)$$

1. Find the exact electron eigenvalues and eigenfunctions for $a = 0$. How do they depend on $\Delta$? (Note that in the case $a = 0$ the non local potential proportional to $\Delta$ commutes with the rest of the hamiltonian).

2. For negative $\Delta$, what is the transition value $\Delta_c$ between an even and an odd ground state wavefunction?

3. For $a \neq 0$, in the limit of infinite mass ( $m \rightarrow \infty$ ) the electron eigenfunctions are clearly localized in space but the electron position is not a well defined quantum number. In fact the two states $|x_0 >$ and

$|-x_0>$ (with the electron at the positions $x_0$ and $-x_0$ respectively) interact owing to the presence of the non local potential proportional to $\Delta$. Find all the electron eigenvalues and eigenfunctions in this limit.

4. Still in the infinite mass limit, what is the condition on the parameters $\Delta$ and $a$ in order for the ground state to have a stable local minimum away from the origin.

## Problem 6
## Absorption spectrum of the HCl molecule

In a far infrared absorption experiment with HCl molecules in their vibrational ground state, it is observed that the following frequencies $\nu = \omega/(2\pi)$, (given here in units of $cm^{-1}$, i.e., as $\nu/c$) are absorbed:

20.68  41.36  62.04  82.72  103.40  124.08  144.76  165.44  186.12  206.80

Assume that only transitions between neighboring energy levels take place (dipole transitions). Be aware of the fact that the first vibrational transition is found at a much higher frequency ($\approx 2880 \, cm^{-1}$).

(a) What kind of states are involved in such transitions?

(b) What are the energy levels of this HCl molecule if the zero of the energy scale is fixed by $E_0 = 0$ ? Give an analytic expression, recognizing the important physical quantities determining the spectrum, and estimate, when appropriate, their values.

(c) Given that a Cl atom is $\approx 35.45$ times heavier then a H atom, and that the Avogadro number is $\approx 6 \cdot 10^{23}$, estimate, from the answer to part (b), the internuclear distance of the HCl molecule.

Numerical values of universal constants: $\hbar \approx 1.0546 \cdot 10^{-28} \, erg\,sec$, $c \approx 2.9979 \cdot 10^{10} \, cm/sec$.

## Problem 7
## Tunneling in presence of a bath of oscillators

A quantum system can tunnel between two different equilibrium configurations decribed by the two orthogonal wavefunctions $|a\rangle$ and $|b\rangle$. The tunneling Hamiltonian can be written as

$$\hat{H}_{\text{tunnel}} = \hbar\Delta\left(|a\rangle\langle b| + |b\rangle\langle a|\right) \equiv \hbar\Delta\hat{\sigma}_x, \tag{1}$$

where the Pauli matrix $\hat{\sigma}_x$ acts in the subspace of the two states.

**1.** – Diagonalize the Hamiltonian (1) assuming $\Delta > 0$. If initially the system is in state $|a\rangle$, what is the probability that, after time $t$, it will be in state $|b\rangle$? Find the tunneling time $\tau$ which the system takes initially to hop in the state $|b\rangle$.

Next, the system is coupled to a bath of harmonic oscillators, which are described by the Hamiltonian

$$\hat{H}_{\text{bath}} = \sum_n \frac{\hbar\omega_n}{2}\left(p_n^2 + x_n^2\right), \tag{2}$$

($x_n$ and $p_n$ being the coordinate and conjugate momentum of the nth oscillator in dimensionless units) through a coupling

$$\hat{V} = \sum_n \hbar\omega_n c_n x_n \hat{\sigma}_z, \tag{3}$$

where $c_n$ are dimensionless coupling constants and $\hat{\sigma}_z = |a\rangle\langle a| - |b\rangle\langle b|$.

**2.** – Solve the model described by the Hamiltonian $\hat{H}_0 = \hat{H}_{\text{bath}} + \hat{V}$, and write explicitly the doubly degenerate lowest energy states.

Now assume that the density of states of the bath is constant and equal to $\rho_0$ up to a high frequency cutoff $D \gg \Delta$, and zero above, and also assume that $c_n = \sqrt{\frac{\alpha}{\rho_0\omega_n}}$, with $\alpha$ a positive dimensionless constant. For finite $\Delta$, there will be a frequency $\omega_0 = \Delta_{eff}$, related to, but not identical with $\Delta$, so that all oscillators with $\omega_n < \omega_0$ are with a good approximation irrelevant, and only those with $\omega_n > \omega_0$ have an effect on the tunneling problem. [The inverse of $2\Delta_{eff}$ is the typical tunneling time $\tau$ of the system in the presence of the bath]. Thus the Hamiltonian can be taken as

$$\hat{H} = \sum_{\omega_n > \Delta_{eff}} \left[\frac{\hbar\omega_n}{2}\left(p_n^2 + x_n^2\right) + \hbar\omega_n c_n x_n \hat{\sigma}_z\right] + \hbar\Delta\hat{\sigma}_x. \tag{4}$$

6

The ground state of (4) is again degenerate for $\Delta = 0$, and will be split by $\Delta$ by an amount $2\hbar\Delta_{eff}$, which, in analogy with the solution of Point 1., is therefore inversely proportional to the effective tunneling time.

**3.** – Use degenerate perturbation theory to find the expression for $\Delta_{eff}$.

**4.** – Show that for $\alpha > 1$, $\Delta_{eff} = 0$, while $\Delta_{eff} \neq 0$ for $\alpha < 1$, and explain the reason in physical terms.