

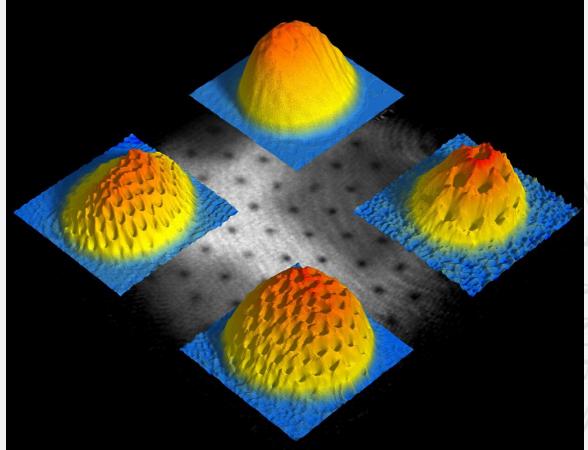


UNIVERSITÀ DEGLI STUDI DI MILANO

Advanced Statistical Physics

Lecture 8

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1



## Outline:

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- Helium quantum liquids, the “permanent” fluids
- Quantum statistical averages: “double” averages
- Statistical mixtures: pure states mixed states
- The density matrix
- Von Neumann entropy
- Quantum statistical ensembles

Scope: to recognize the necessity of a quantum statistical formalism/approach; introduction to the formalism which allows for the inclusion of statistical treatment of many-body quantum systems

*VEDIAMO UN SIST. CHE NECESSITA DELLA F. QUANTISTICA*

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2

2

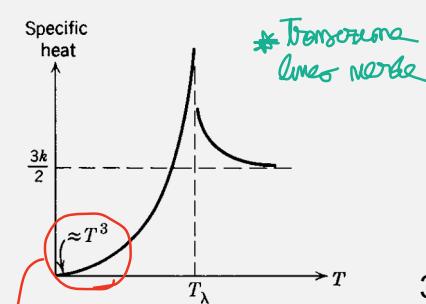
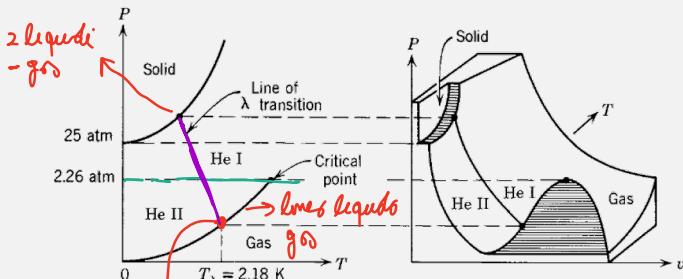
## The "lambda" transition *also: scarpice ma leggero*

- The thermodynamic surface of  ${}^4\text{He}$  is shown in figure.
- In the liquid phase there is continuous phase transition dividing the liquid further into He I and He II. The former is a normal-type liquid, but He II exhibits superfluid behavior

*\*oss: la fase solida non offre o  
meno di 25 atm  $\rightarrow$  mentre allo zero si raffredda nulla  
 $\hookrightarrow$  lo liquido entra in nullo*

- The specific heat diverges as  $T_\lambda$  is approached from either sides
- The shape of the specific-heat curve near  $T_\lambda$  gives rise to the name  $\lambda$  transition

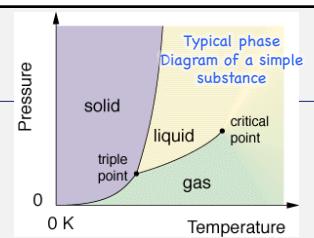
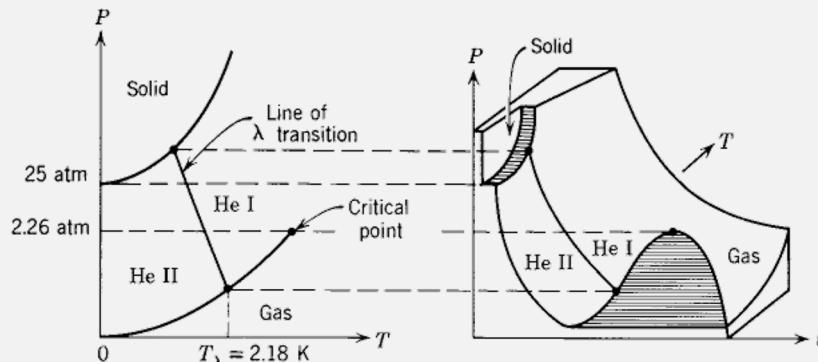
*$\hookrightarrow$  lo liquido nulla è tutta una linea orizzontale*



*\*Transizione linea nera*

*decrescere  
fornire  
 $\rightarrow$  scaricazioni del g.s.  
sono portate quelle  
energetiche superiori*

## The Helium phase diagrams

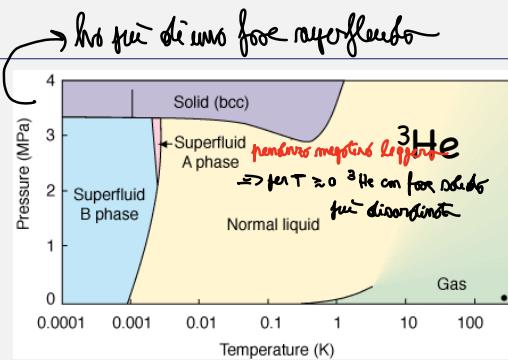
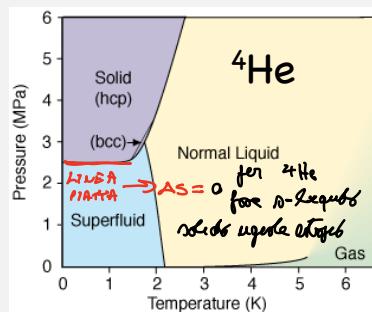


- ${}^4\text{He}$  has 2 protons and 2 neutrons in the nucleus with 2 electrons around; each of these spin 1/2 particles has its pair, so that the total spin of the  ${}^4\text{He}$  atom is zero: **Boson**. No significant magnetic properties

- ${}^3\text{He}$  (2 protons but only 1 neutron) has a net nuclear spin of 1/2 because of the unpaired neutron: **Fermion**

*un bos  
metrone di  
differenza  
l'atomo solo  
4*

## The permanent liquids!



- ${}^3\text{He}$  is an almost ideal "spin 1/2 solid" with 2 possible nuclear spin states per atom. This leads to a lot of disorder in the solid ( $k_B \ln 2$  per atom) which persists to really quite low temperature: the spins are sufficiently weakly interacting that the spin disorder is not frozen out until around 1 mK
- ${}^3\text{He}$  follows the Fermi-Dirac statistics; in the liquid phase the heat capacity is linear in temperature ( $C = T \partial S / \partial T \Rightarrow S \sim T$ )  $\Rightarrow$  the solid below 0.3 K is more disordered than the liquid! ✓
- At very low T the solid and the liquid have the same entropy (Clausius-Clapeiron equation:  $dP/dT = \Delta s / \Delta V \Rightarrow dP/dT = 0 \Rightarrow \Delta s = 0$ )

5

5

\* questo perché mentre Fermioni nello stato liquido sono legate a determinate energie Fermi-Direc  
↳ molti orbitali  
mentre nel solido gli atomi possono utilizzare Fermi-Direc sarebbero sui reticolli benuti → più disponibili

## Quantum fluids

- A **quantum fluid** is a substance which remains fluid at such "low" temperature that the effects of quantum mechanics (quantum statistics) play a dominant role
- Rare gas inter-atomic potential: short range repulsion and long range van der Waals attraction:

$$V(r) = a e^{-br} - \frac{C}{r^6}$$

$$V_{LJ}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

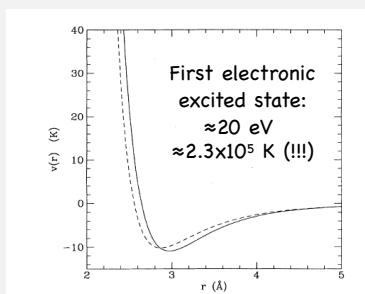
- Hamiltonian:

$$H = T + U = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + U(\vec{r}_1, \dots, \vec{r}_N) + (H_{\text{dipole}}) \text{ only for } {}^3\text{He}$$

$$U(\vec{r}_1, \dots, \vec{r}_N) = \sum_{i < j}^N V(\vec{r}_i - \vec{r}_j) + U_3 + \dots$$

$\approx 10^{-2} K$

$\approx 10^{-7} K$



The semiempirical pair potential between two helium atoms: solid line, Aziz *et al.* (1992); dashed line, Lennard-Jones 6-12 potential with  $\epsilon = 10.22 \text{ K}$  and  $\sigma = 2.556 \text{ \AA}$ .

distanze molto piccole

Momento termico a fine di 2 corpi  $\rightarrow$   
e termini di dipolo

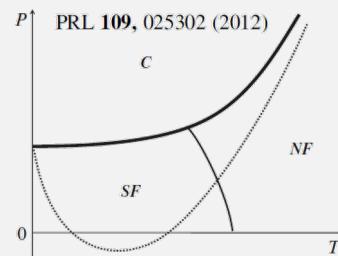
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6

## Why is there no solid?

- In Helium atoms are sufficiently loosely bound by the weak van der Waals forces that even this zero point motion is enough to make the solid phase unstable, i.e. it melts under its own zero point energy
- Very recently, however, it has been recognized that also Bose statistics play an important role  
 $\hookrightarrow$  è importante l'indistinguibilità
- Only when the solid is stiffened by pressure it becomes the stable phase
- Why there is no gas? The ground state of  $^3\text{He}$  and  $^4\text{He}$  atoms is a liquid droplet... how many atoms are needed to form a droplet?  $N_c \approx 2$  for  $^4\text{He}$  (binding energy  $\approx 1 \text{ mK}$ ),  $N_c \approx 40$  for  $^3\text{He}$

sono così leggeri che il gr di indistinguibilità rompe i reticolli dei solidi  
 $\hookrightarrow$  corretto



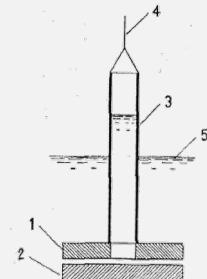
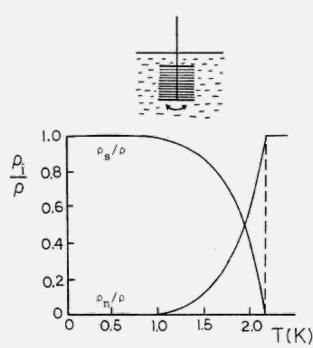
Schematic liquid-solid phase diagram for Lennard-Jones type Bose systems. Solid lines separate the normal fluid (NF), superfluid (SF), and crystalline (C) phases. The dashed line shows the position of the crystal-liquid boundary if quantum exchanges are neglected. In case of  $^4\text{He}$  mass and potential, distinguishable particles predict a solid phase around  $T = 0.5 \text{ K}$ . Phases at  $P < 0$  are metastable as vapor (excluded here for clarity) is the equilibrium state at finite temperature and zero pressure. Note that in the  $T \rightarrow 0$  limit the descriptions in terms of distinguishable and Bose particles become equivalent

7

7

## Viscosity in He-II

- Flow of HeII through very fine capillaries indicates a vanishingly small viscosity, at least  $10^{11}$  times smaller than HeI: superfluidity of liquid helium
- For not too great pressures, the velocity of flow through these fine capillaries appears independent of the pressure head and is greater in tubes of smaller diameter



- Andronikashvili's experiment (oscillating disc viscometer): only a part of the fluid is dragged by discs "normal component"

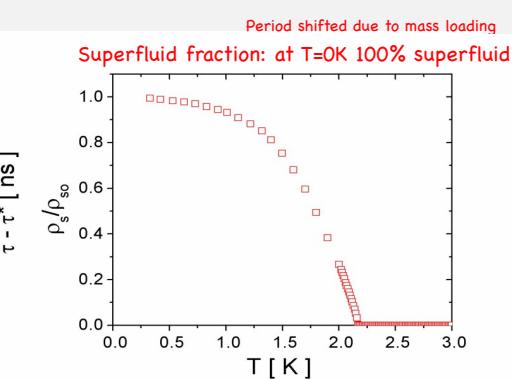
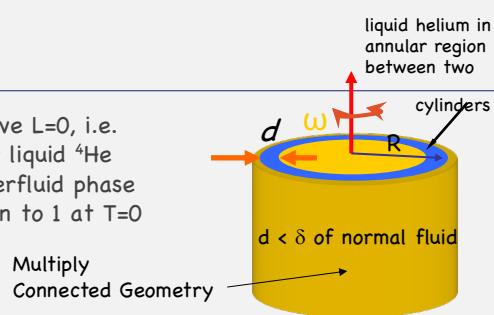
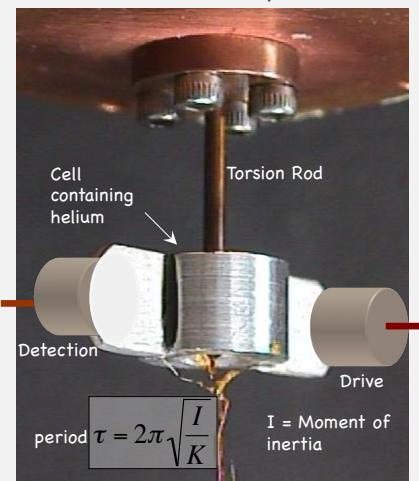
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8



## Torsional oscillator experiment

- For  $\rho_s/\rho=0$  the system is normal, while for  $\rho_s/\rho=1$  we have  $L=0$ , i.e. the system stays at rest in the lab. Experimentally, for liquid  $^4\text{He}$   $\rho_s/\rho$  is zero in the normal phase; as we go into the superfluid phase it increases continuously from 0 at the lambda transition to 1 at  $T=0$



9

*↳ muore lo ruotato ridendo quindi il fluido segue le oscillazioni di vibrazione dell'oggetto  $\Rightarrow$  a  $T=0\text{ K}$  ha solo legge di rotazione*

9

## The density matrix, statistical mixture

- The starting point of classical statistical mechanics is the realization that **a system can assume many microstates for given macroscopic (thermodynamic) state quantities**.
- The quantum-mechanical description, based on an incomplete set of data concerning the system, is obtained by means of what is called a **density matrix**. The knowledge of this matrix enables us to calculate the mean value of any quantity describing the system
- Suppose we have the possibility to prepare a quantum (many-body) system in a specific microstate, and consider two different ways of preparing the microstate of a system at time  $t_0$ :

$$|\psi_1(t_0)\rangle; |\psi_2(t_0)\rangle$$

- Imagine that a given **statistical experiment** corresponds to the measurement of the properties of this system prepared  $N_1$  times in the state  $|\psi_1(t_0)\rangle$  and  $N_2$  times in the state  $|\psi_2(t_0)\rangle$  with  $N=N_1+N_2$ ,  $N_1$  and  $N_2$  sufficiently large
- Such procedure corresponds to the **statistical mixture** of preparations  $|\psi_1(t_0)\rangle$  and  $|\psi_2(t_0)\rangle$  with statistical weight  $\rho_1=N_1/N$  and  $\rho_2=N_2/N$ ;  $\rho_1, \rho_2 > 0$ ;  $\rho_1+\rho_2=1$



10

10

- The corresponding **statistical prediction** for an observable  $A$  at time  $t$  becomes

$$\langle \hat{A} \rangle_t = \sum_{i=1}^n \rho_i \langle \psi_i(t) | \hat{A} | \psi_i(t) \rangle$$

- This situation, that at first sight could seem artificial, is very realistic: think about how difficult could be, for a macroscopic quantum system, to control exactly its energy, the number of particles which constitute it, and so on ...
- It is therefore perfectly natural the following obvious extension: if the microstate of a quantum system can be prepared at time  $t_0$  in the state  $|\psi_\lambda(t_0)\rangle$ , where  $\lambda$  is a parameter (for example, connected to control devices) with statistical weight  $\rho(\lambda)d\lambda$  in the interval  $[\lambda, \lambda+d\lambda]$  such that  $\rho(\lambda) \geq 0 \forall \lambda$  and  $\int d\lambda \rho(\lambda) = 1$ , the statistical prediction for an observable at time  $t$  becomes

$$\begin{aligned} \langle \hat{A} \rangle_t &= \int d\lambda \rho(\lambda) \langle \psi_\lambda(t) | \hat{A} | \psi_\lambda(t) \rangle = \\ &= \int d\lambda \rho(\lambda) \langle \psi_\lambda(t_0) | e^{\frac{i}{\hbar} \hat{H}(t-t_0)} \hat{A} e^{-\frac{i}{\hbar} \hat{H}(t-t_0)} | \psi_\lambda(t_0) \rangle \end{aligned}$$

or the discrete version

$$\langle \hat{A} \rangle_t = \sum_{\lambda} \rho_{\lambda} \langle \psi_{\lambda}(t) | \hat{A} | \psi_{\lambda}(t) \rangle \quad \text{with} \quad \rho_{\lambda} \geq 0 \forall \lambda; \quad \sum_{\lambda} \rho_{\lambda} = 1$$

11

11

*per cui ancora progetto classico  $\Rightarrow$  frutto dei nuclei macroscopici*

## Quantum statistical averages

- Thus in **quantum statistical mechanics**, where the observer has an incomplete knowledge about the preparation of a quantum system, one is no longer able to tell which specific microstate  $|\psi_i\rangle$  the system is prepared and can give only a probability  $\rho_i$  of finding the system prepared in a particular microstate  $|\psi_i\rangle$ .
- We note that the states  $|\psi_i\rangle$  are not necessarily orthogonal.
- Thus **another average adds** to the usual intrinsic quantum mechanical average.
- If one now performs a measurement of the observable  $A$ , one can measure only the average of the quantum mechanical expectation values, weighted by the probabilities  $\rho_i$

$$\langle \hat{A} \rangle = \sum_i \rho_i \langle \psi_i | \hat{A} | \psi_i \rangle$$

qui non bis unica quantità  
perche non ha rappresentazione

- However, the previous expression is not the **most general expression** for a quantum statistical average.

12

12

## The density matrix: $\rho_{kk'}$

- In fact, expanding the states  $|\psi_i\rangle$  with respect to a complete set  $|\phi_k\rangle$  we obtain

$$\begin{aligned} |\psi_i\rangle &= \sum_k a_k^i |\phi_k\rangle \\ \langle \hat{A} \rangle &= \sum_i \rho_i \sum_{k,k'} a_k^{i*} a_{k'}^i \langle \phi_k | \hat{A} | \phi_{k'} \rangle = \sum_{k,k'} \left( \sum_i \rho_i a_k^{i*} a_{k'}^i \right) \langle \phi_k | \hat{A} | \phi_{k'} \rangle \\ \Rightarrow \quad \langle \hat{A} \rangle &= \sum_{k,k'} \rho_{kk'} \langle \phi_k | \hat{A} | \phi_{k'} \rangle \end{aligned}$$

come tenere

- The most general expression involves the **density matrix**:  $\rho_{kk'}$  **mette**

13

13

## The density operator

- One can now interpret the numbers  $\rho_{kk'} := \sum_i \rho_i a_k^{i*} a_{k'}^i$

as the **matrix elements of an operator**,  $\hat{\rho}$ , in the basis of the  $|\phi_k\rangle$ ,

$$\langle \hat{A} \rangle = \sum_{k,k'} \rho_{kk'} \langle \phi_k | \hat{A} | \phi_{k'} \rangle = \sum_{k,k'} \langle \phi_{k'} | \hat{\rho} | \phi_k \rangle \langle \phi_k | \hat{A} | \phi_{k'} \rangle = \sum_{k'} \langle \phi_{k'} | \hat{\rho} \hat{A} | \phi_{k'} \rangle = \text{Tr}(\hat{\rho} \hat{A})$$

- The **trace**,  $\text{Tr}(\bullet)$ , is just the sum of the expectation values of the operator (diagonal matrix elements) in an arbitrary basis:

$$\text{Tr}(\hat{O}) = \sum_{k'} \langle \phi_{k'} | \hat{O} | \phi_{k'} \rangle$$

- The value of the **trace is independent of the basis chosen**, since given  $|\phi_k\rangle = \sum_i S_{ki} |\varphi_i\rangle$  (Unitarity ( $S^* S = S S^* = I$ ) of the basis transformation  $S$  is required) it follows that

$$\text{Tr}(\hat{O}) = \sum_k \langle \phi_k | \hat{O} | \phi_k \rangle = \sum_{k,j} S_{ki}^* S_{kj} \langle \varphi_i | \hat{O} | \varphi_j \rangle = \sum_{i,j} \delta_{ij} \langle \varphi_i | \hat{O} | \varphi_j \rangle = \sum_i \langle \varphi_i | \hat{O} | \varphi_i \rangle$$

14

14

## Properties of the density matrix

- From the definition of the matrix elements of the density matrix in an arbitrary basis,

$$\rho_{kk'} = \sum_i \rho_i a_k^{i*} a_{k'}^i$$

since the  $\rho_i$  are real, it follows immediately that **the density matrix is Hermitian**

$$\rho_{k'k}^* = \rho_{kk'} \quad \hat{\rho}^+ = \hat{\rho}$$

- From the normalization,  $\sum_i \rho_i = 1$ , one concludes that

$$\text{Tr}(\hat{\rho}) = \sum_k \langle \phi_k | \hat{\rho} | \phi_k \rangle = \sum_k \rho_{kk} = \sum_i \rho_i \left( \sum_k |a_k^i|^2 \right) = \sum_i \rho_i = 1$$

- Let us discuss the physical meaning of the matrix elements of the density operator...

15

15

- We can see that the diagonal term

$$\rho_{kk} = \sum_i \rho_i |a_k^i|^2 = \sum_i \rho_i \langle \psi_i | \phi_k \rangle \langle \phi_k | \psi_i \rangle = \text{Tr}(\hat{\rho} \hat{P}_k) \quad \text{with} \quad \hat{P}_k = |\phi_k\rangle\langle\phi_k|$$

represents the probability that the system is in the state  $|\phi_k\rangle$  after measuring the observable whose eigenstates are  $\{|\phi_k\rangle\}$ . For this reason  $\rho_{kk}$  represents the “**population**” (occup. prob.) of the state  $|\phi_k\rangle$ .

- The off-diagonal terms  $\rho_{kk'}$  represent interference between the states  $|\phi_k\rangle$  and  $|\phi_{k'}\rangle$ .
- Such interference is present for any state  $|\psi_i\rangle$  of the statistical mixture containing a linear superposition of  $|\phi_k\rangle$  and  $|\phi_{k'}\rangle$ .
- We can see that  $\rho_{kk'}$ , for  $k \neq k'$ , is a weighted sum of the interference terms

$$\rho_{kk'} = \sum_i \rho_i a_k^{i*} a_{k'}^i = \sum_i \rho_i \langle \psi_i | \phi_k \rangle \langle \phi_{k'} | \psi_i \rangle$$

16

16

- We stress that the individual terms appearing in this sum are complex quantities and, therefore,  $\rho_{kk'}$  can be equal to zero even though the individual terms are not.
- If  $\rho_{kk'} = 0$ , then, even after averaging over the statistical mixture, a quantum-coherence effect between the states  $|\phi_k\rangle$  and  $|\phi_{k'}\rangle$  will remain. For this reason the off-diagonal elements of the density matrix are known as **coherences**. Physical origin of coherences: given a state  $|\psi_i\rangle$  with  $\rho_i \neq 0$ , coherences are present between  $|\phi_k\rangle$  and  $|\phi_{k'}\rangle$  if

$$\langle \phi_k | \psi_i \rangle \neq 0 \neq \langle \phi_{k'} | \psi_i \rangle$$

- Actually, since the density operator is Hermitian, non-negative and has unit trace, it is always possible to find an orthonormal basis of eigenstates of the density operator such that

$$\hat{\rho} = \sum_i \rho_i |\varphi_i\rangle\langle\varphi_i|; \quad 0 \leq \rho_i \leq 1; \quad \sum_i \rho_i = 1; \quad \hat{\rho}|\varphi_i\rangle = \rho_i |\varphi_i\rangle$$

- This implies that the density matrix can always be seen as a statistical mixture of the states without coherences between them, even though these states are not, in general, eigenstates of a physical observable.

17

17

## Statistical and quantum averages

- Assume the state vector  $|\Psi\rangle$  of the system exactly known, and represented by the following linear combination  $|\Psi\rangle = \sum_i a_i |\psi_i\rangle$ .  $a_i$  are complex numbers.
- The quantum mechanical expectation value of an observable now reads

$$\langle \Psi | \hat{A} | \Psi \rangle = \sum_{i,j} a_i^* a_j \langle \psi_i | \hat{A} | \psi_j \rangle$$

- However, if one forms the purely statistical average in a mixed state, where the  $|\psi_i\rangle$  just appear with the probabilities  $\rho_i$ ,

$$\langle \hat{A} \rangle = \sum_i \rho_i \langle \psi_i | \hat{A} | \psi_i \rangle$$

- Mixed terms are not present in the latter case. Even if one prepares a system in such a way that in the mixed state the  $\rho_i$  correspond exactly to the  $|a_i|^2$ , nevertheless in general one does not obtain the same average, since information about the phases of  $a_i$  is not contained in the statistical average. The statistical mixture of the states  $|\psi_i\rangle$ , with weights  $\rho_i$ , should not be confused with the linear superposition

18

18

## Pure and mixed states

- If a quantum mechanical system is in a certain microstate, described by a state vector  $|\psi_i\rangle$  we say it is in a **pure state**.
- If on the other hand the system has been prepared as a statistical mixture of microstates  $|\psi_i\rangle$  with probabilities  $p_i$  we are dealing with a **mixed state**
- The mixed, as well as pure, states can be completely described by the matrix elements of a **density operator**; i.e., all quantum mechanical and statistical quantum averages of arbitrary observables can be calculated if the density matrix is known
- To this end, we first denote the density operator in an arbitrary basis  $|\phi_k\rangle$  in Dirac's notation:

$$\rho_{kk'} := \langle \phi_{k'} | \hat{\rho} | \phi_k \rangle \Rightarrow \hat{\rho} = \sum_{k,k'} |\phi_{k'}\rangle \rho_{kk'} \langle \phi_k|$$

- If we prepare our system in a **pure state**, i.e. in such a way that it may be in only one of the states  $|\psi_i\rangle$ , for example  $i=l$ , with the probabilities  $p_{ll}=1$ ,  $p_{ii}=0 \forall i \neq l$  and  $p_{ik}=0$  for  $i \neq k$ , the density operator is

$$\hat{\rho} = |\psi_l\rangle \langle \psi_l|$$

19

19

- For **mixed states**, several terms contribute to the previous sum; i.e., one cannot exactly determine the state that the system assumes. Note that the states  $|\psi_i\rangle$  of a statistical mixture are not necessarily complete in the full Hilbert space. They just span the subspace of the Hilbert space in which the state vector is not precisely determinable
- However, note that with respect to an **arbitrary basis**, the density matrix of a pure state may contain many matrix elements which are different from zero

$$\hat{\rho}_{pure} = |\psi_i\rangle \langle \psi_i| = \sum_{kk'} |\phi_{k'}\rangle \langle \phi_{k'}| \langle \psi_i | \phi_k \rangle \langle \phi_k| = \sum_{kk'} |\phi_{k'}\rangle a_k^{i*} a_{k'}^i \langle \phi_k| \Rightarrow \rho_{kk'}^{pure} = a_k^{i*} a_{k'}^i$$

- From the general properties of projection operators,  $P^2=P$  since  $|\psi_i\rangle \langle \psi_i| = |\psi_i\rangle \langle \psi_i| \psi_i \rangle \langle \psi_i|$  a convenient **criterion** follows for the case when the density matrix describes a pure state. In this case it must be valid, independent of the basis, that

- If the system is in a **pure state** then **statistical quantum averages correspond to ordinary quantum averages**:

$$\hat{\rho}_{pure}^2 = \hat{\rho}_{pure}$$

$$\langle \hat{A} \rangle_{stat} = \text{Tr}(\hat{\rho}^{pure} \hat{A}) = \sum_k \langle \phi_k | \psi_i \rangle \langle \psi_i | \hat{A} | \phi_k \rangle = \sum_k \langle \psi_i | \hat{A} | \phi_k \rangle \langle \phi_k | \psi_i \rangle = \langle \psi_i | \hat{A} | \psi_i \rangle = \langle \hat{A} \rangle_{quantum}$$

20

20

## The von Neumann entropy

- It is interesting to associate to a density operator a quantity which indicates the degree of mixing; this quantity is the **von Neumann entropy**, and is defined as

$$S(\hat{\rho}) = -Tr(\hat{\rho} \log \hat{\rho}) = -\langle \log \hat{\rho} \rangle$$

- From the spectral representation of the density operator it follows that

$$\hat{\rho} = \sum_i |\psi_i\rangle \rho_i \langle \psi_i| \Rightarrow \hat{\rho} \log(\hat{\rho}) = \sum_i |\psi_i\rangle \rho_i \log \rho_i \langle \psi_i|$$

thus

$$S(\hat{\rho}) = -\sum_i \rho_i \log \rho_i$$

- The von Neumann entropy is thus the quantum analogue of the Shannon entropy; it inherits the properties connected with its functional form: the von Neumann entropy is large when the eigenvalues of the density operator are small; given the normalization condition  $\sum_i \rho_i = 1$  this corresponds to strong mixing. Increasing values of the von Neumann entropy thus indicate an increasing degree of mixing

21

21



- The von Neumann entropy satisfies also the following properties:  $S(\hat{\rho}) = 0$  for a pure state. Indeed, in this case only one eigenvalue of the density operator is different from zero, say  $\rho_1 = 1$ , so that

$$S(\hat{\rho}) = -\sum_i \rho_i \log \rho_i = -\rho_1 \log \rho_1 = 0$$

- The entropy is not modified by a unitary change of basis; that is,  $S(U\hat{\rho}U^+) = S(\hat{\rho})$

Actually  $S(\hat{\rho})$  depends only on the eigenvalues of the density operator which are basis-independent. This property means that the von Neumann entropy is invariant under unitary temporal evolution.

- If the density operator  $\rho$  acts on a  $M$ -dimensional Hilbert space, then

$$0 \leq S(\hat{\rho}) \leq \log M$$

It is easy to see that  $S(\hat{\rho}) \geq 0$  since  $0 \leq \rho_i \leq 1$  and therefore  $-\rho_i \log \rho_i \geq 0$ . To show that  $S(\hat{\rho}) \leq \log M$  we remember that the Shannon entropy takes its maximum value  $\log M$  when  $\rho_1 = \dots = \rho_N = 1/M$ . Hence

$$S(\hat{\rho}) \leq -\frac{1}{M} \sum_{i=1}^M \log \frac{1}{M} = \log M$$

22

22

- Consider now a system, divided in **two subsystems**, which has been **prepared as a statistical mixture** which consists of **independent preparations of the two subsystem**. This situation can be modelled with a Hilbert space which is the tensor product of two Hilbert spaces  $H=H_1\otimes H_2$ , one for each subsystem, with a density operator of the form

$$\text{which means } \hat{\rho} = \hat{\rho}_1 \otimes \hat{\rho}_2 \quad \hat{\rho}|\phi^{(1)},\phi^{(2)}\rangle = |\hat{\rho}^{(1)}\phi^{(1)},\hat{\rho}^{(2)}\phi^{(2)}\rangle$$

The eigenstates of the density operator are of the form

$$|\psi_i^{(1)},\psi_j^{(2)}\rangle ; \quad \hat{\rho}^{(1)}|\psi_i^{(1)}\rangle = \rho_i^{(1)}|\psi_i^{(1)}\rangle ; \quad \hat{\rho}^{(2)}|\psi_j^{(2)}\rangle = \rho_j^{(2)}|\psi_j^{(2)}\rangle$$

$$\text{It follows that } \hat{\rho}|\psi_i^{(1)},\psi_j^{(2)}\rangle = \rho_i^{(1)}\rho_j^{(2)}|\psi_i^{(1)},\psi_j^{(2)}\rangle$$

$$\begin{aligned} S(\hat{\rho}^{(1)} \otimes \hat{\rho}^{(2)}) &= -\sum_{i,j} \rho_i^{(1)} \rho_j^{(2)} \log \rho_i^{(1)} \rho_j^{(2)} = -\sum_i \rho_i^{(1)} \log \rho_i^{(1)} \sum_j \rho_j^{(2)} - \sum_j \rho_j^{(2)} \log \rho_j^{(2)} \sum_i \rho_i^{(1)} = \\ &= -\sum_i \rho_i^{(1)} \log \rho_i^{(1)} - \sum_j \rho_j^{(2)} \log \rho_j^{(2)} = S(\hat{\rho}^{(1)}) + S(\hat{\rho}^{(2)}) \end{aligned}$$

thus the absence of statistical correlation in the preparation of the two subsystem implies additivity of the entropy

23

23

## Time evolution

- Consider the **time evolution of the density matrix**: we allow for a temporal change of the statistical mixture prepared with the states  $|\psi_i(t)\rangle$ , over which one has to average, with the probabilities  $\rho_i$ . Each  $|\psi_i(t)\rangle$  fulfills the Schrödinger equation and its Hermitian conjugate

$$i\hbar \frac{\partial}{\partial t} |\psi_i(t)\rangle = \hat{H} |\psi_i(t)\rangle \quad -i\hbar \frac{\partial}{\partial t} \langle \psi_i(t)| = \langle \psi_i(t)| \hat{H}$$

- $\rho_i$  do not change with time: they merely determine how we prepared the system at  $t_0$ . Afterwards, the system evolves according to its Hamiltonian, and the  $\rho_i$  will stay constant as long as one does not interfere from outside. We obtain

$$i\hbar \frac{d\hat{\rho}}{dt} = i\hbar \frac{d}{dt} \sum_i |\Psi^i(t)\rangle \rho_i \langle \Psi^i(t)| = \sum_i \left\{ \hat{H} |\Psi^i(t)\rangle \rho_i \langle \Psi^i(t)| - |\Psi^i(t)\rangle \rho_i \langle \Psi^i(t)| \hat{H} \right\} = \hat{H}\hat{\rho} - \hat{\rho}\hat{H}$$

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}]$$

This is the **von Neumann's equation**. It is the analogy to the **Liouville** equation for the classical phase-space density

24

24

## Choosing the density operator

- The choice of the density operator representing a particular preparation of a quantum system is done by considering a set of observables and the correspondent expectation values
- A density operator is uniquely determined from the set of its expectation values. In fact given two density operators  $\hat{\rho}_1; \hat{\rho}_2$   
such that  $\text{Tr}(\hat{\rho}_1 \hat{A}) = \langle \hat{A} \rangle = \text{Tr}(\hat{\rho}_2 \hat{A}) \quad \forall \hat{A} \Rightarrow \text{Tr}[(\hat{\rho}_1 - \hat{\rho}_2) \hat{A}] = 0$   
*valori medi*  
one can take  $\hat{A} = |\varphi\rangle\langle\varphi|$ , i.e. the density operator of a pure state  
to obtain  $\text{Tr}[(\hat{\rho}_1 - \hat{\rho}_2) \hat{A}] = \langle \varphi | \hat{\rho}_1 - \hat{\rho}_2 | \varphi \rangle = 0 \quad \forall |\varphi\rangle \Rightarrow \hat{\rho}_1 = \hat{\rho}_2$
- For many-body quantum systems only a particular subset  $M$  of “relevant” (macroscopic) observables can be, usually, measured. We consider now the set  $\Sigma_M$  of the density operators that give the correct expectation values for such observables:

$$\hat{\rho} \in \Sigma_M \Leftrightarrow \text{Tr}[\hat{\rho} \hat{A}_i] = a_i \quad \forall \hat{A}_i \in M$$

25

25

- We are induced to search for the  $\hat{\rho}$  in  $\Sigma_M$  which maximize the von Neumann entropy; from the physical point of view, this density operator represents better the non-relevance of the observables excluded by our knowledge
- Consider the operator  $e^{-\sum_i \lambda_i \hat{A}_i}$  such that  $\text{Tr}(e^{-\sum_i \lambda_i \hat{A}_i}) < \infty$   
and that  $a_i = \frac{\text{Tr}(e^{-\sum_i \lambda_i \hat{A}_i} \hat{A}_i)}{\text{Tr}(e^{-\sum_i \lambda_i \hat{A}_i})}$   
it follows that the density operator  $\hat{\rho} = \frac{e^{-\sum_i \lambda_i \hat{A}_i}}{\text{Tr}(e^{-\sum_i \lambda_i \hat{A}_i})} \in \Sigma_M$
- One can prove this in two steps; the first step is that given two generic density operators the following inequality holds:  

$$\text{Tr}(\hat{\rho}' \log \hat{\rho}') \geq \text{Tr}(\hat{\rho} \log \hat{\rho})$$

the equality holds iff the two density operators are equal. In fact, given the spectral representation of a density operator

$$\hat{\rho} = \sum_i \rho_i |\psi_i\rangle\langle\psi_i| ; \quad \sum_i |\psi_i\rangle\langle\psi_i| = 1$$

26

26

We have  $\text{Tr}[\hat{\rho}'(\log \hat{\rho} - \log \hat{\rho}')]=\sum_i \rho'_i \langle \psi'_i | \log \hat{\rho} - \log \rho'_i | \psi'_i \rangle =$

27

(Note that in the last expression we are adding only on the index  $i$  such  $\rho'_i \neq 0$ ; moreover, in writing  $\text{Tr}(\hat{\rho}' \log \hat{\rho})$  we are assuming that  $\langle \psi'_i | \hat{\rho} | \psi'_i \rangle \neq 0 \forall i : \rho'_i \neq 0$ )

$$\begin{aligned} &= \sum_i \rho'_i \left\langle \psi'_i \left| \log \frac{\hat{\rho}}{\rho'_i} \right| \psi'_i \right\rangle = \sum_{i,j} \rho'_i \left\langle \psi'_i \left| \log \frac{\rho_j}{\rho'_i} \right| \psi_j \right\rangle \langle \psi_j | \psi'_i \rangle \\ &\stackrel{(\log x \leq x-1)}{\leq} \sum_{i,j} \rho'_i \left\langle \psi'_i \left| \frac{\rho_j}{\rho'_i} - 1 \right| \psi_j \right\rangle \langle \psi_j | \psi'_i \rangle = \sum_i \rho'_i \left\langle \psi'_i \left| \frac{\hat{\rho}}{\rho'_i} - 1 \right| \psi'_i \right\rangle = \text{Tr}(\hat{\rho}) - \text{Tr}(\hat{\rho}') = 0 \end{aligned}$$

- Thus taking  $\hat{\rho}' \in \Sigma_M$  and  $\hat{\rho} = \frac{e^{-\sum_i \lambda_i \hat{A}_i}}{\text{Tr}(e^{-\sum_i \lambda_i \hat{A}_i})}$

$$\begin{aligned} S(\hat{\rho}') &= -\text{Tr}(\hat{\rho}' \log \hat{\rho}') \leq -\text{Tr}(\hat{\rho}' \log \hat{\rho}) = \text{Tr} \left\{ \hat{\rho}' \left[ \sum_i \lambda_i \hat{A}_i + \log \text{Tr}(e^{-\sum_i \lambda_i \hat{A}_i}) \right] \right\} = \\ &= \sum_i \lambda_i a_i + \log \text{Tr}(e^{-\sum_i \lambda_i \hat{A}_i}) = -\text{Tr}(\hat{\rho} \log \hat{\rho}) = S(\hat{\rho}) \end{aligned}$$

- This density operator is, therefore, the natural candidate to describe the statistical mixture characterized by the knowledge of the average values of the relevant observables (the set  $M$ )

## Quantum statistics: canonical ensemble

- The simplest situation correspond to the case in which  $M$  contains only one observable. For example, in the case of  $N$  particles in a box of volume  $V$  one can imagine to perform the preparation controlling only the average value of the Hamiltonian:

$$\hat{A}_{I=1} = \hat{H} \quad \langle \hat{H} \rangle = \varepsilon$$

the density operator which maximizes the von Neumann entropy is given by

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Z} ; \quad Z = \text{Tr}(e^{-\beta \hat{H}})$$

which is the **canonical** density operator; the statistical mixture which corresponds to this preparation is called **canonical ensemble**

- Note that, given the von Neumann's equation  $\hat{\rho} = e^{-\beta \hat{H}} \Rightarrow [\hat{\rho}, \hat{H}] = 0 \Rightarrow \frac{\partial \hat{\rho}}{\partial t} = 0$  i.e. the density operator is time independent.
- **The Equilibrium:** averages values of the relevant variables are time independent  $\Rightarrow$  the density operator cannot explicitly depend on time and, via the von Neumann's equation it must be that  $\frac{\partial \hat{\rho}}{\partial t} = 0 = [\hat{\rho}, \hat{H}] = 0$

## The temperature

- We try now to give a **physical interpretation** of the **parameter  $\beta$**  in

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Z} ; \quad Z = \text{Tr}(e^{-\beta \hat{H}})$$

- As seen in a previous lecture, the constant  $\beta$  is constrained by our knowledge about the average

$$-\frac{\partial \log Z}{\partial \beta} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \text{Tr}(e^{-\beta \hat{H}}) = \text{Tr}(\hat{\rho} \hat{H}) = \langle \hat{H} \rangle = \varepsilon$$

- Consider a **quantum system which consists of two weakly interacting subsystems**: these subsystems are in contact (can exchange energy) but we can write the total energy of the system as the sum of the energies of the sub-systems, i.e. **the interaction energy constitutes a surface contribution which can be neglected respect to volume contributions**

- As discussed previously, this situation can be modelled with a Hilbert space which is the tensor product of two Hilbert spaces  $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$ , one for each subsystem, with a density operator of the form

$$\hat{\rho} = \hat{\rho}_1 \otimes \hat{\rho}_2$$

29

29

- Taken as a basis of this Hilbert space the tensor product of the eigenvalues of the Hamiltonians of the two subsystems  $|n,m\rangle = |n\rangle \otimes |m\rangle$ , we see that

$$\begin{aligned} \text{Tr}(e^{-\beta(\hat{H}_1 + \hat{H}_2)}) &= \sum_{n,m} \langle n,m | e^{-\beta(\hat{H}_1 + \hat{H}_2)} | n,m \rangle = \sum_{n,m} e^{-\beta(E_n + E_m)} = \\ &= \sum_n e^{-\beta E_n} \sum_m e^{-\beta E_m} = \sum_n \langle n | e^{-\beta \hat{H}_1} | n \rangle \sum_m \langle m | e^{-\beta \hat{H}_2} | m \rangle = \text{Tr}(e^{-\beta \hat{H}_1}) \text{Tr}(e^{-\beta \hat{H}_2}) \end{aligned}$$

- Thus  $\hat{\rho} = \frac{e^{-\beta \hat{H}}}{\text{Tr}(e^{-\beta \hat{H}})} = \frac{e^{-\beta(\hat{H}_1 + \hat{H}_2)}}{\text{Tr}(e^{-\beta(\hat{H}_1 + \hat{H}_2)})} = \frac{e^{-\beta \hat{H}_1}}{\text{Tr}(e^{-\beta \hat{H}_1})} \frac{e^{-\beta \hat{H}_2}}{\text{Tr}(e^{-\beta \hat{H}_2})}$

and it follows that

$$\begin{aligned} \langle \hat{H} \rangle &= \text{Tr} \left( \frac{e^{-\beta \hat{H}_1}}{\text{Tr}(e^{-\beta \hat{H}_1})} \frac{e^{-\beta \hat{H}_2}}{\text{Tr}(e^{-\beta \hat{H}_2})} (\hat{H}_1 + \hat{H}_2) \right) = \\ &= \text{Tr} \left( \frac{e^{-\beta \hat{H}_1}}{\text{Tr}(e^{-\beta \hat{H}_1})} \hat{H}_1 \right) + \text{Tr} \left( \frac{e^{-\beta \hat{H}_2}}{\text{Tr}(e^{-\beta \hat{H}_2})} \hat{H}_2 \right) = \langle \hat{H}_1 \rangle + \langle \hat{H}_2 \rangle \end{aligned}$$

30

30

$$\hat{\rho} = \frac{e^{-\beta\hat{H}}}{Tr(e^{-\beta\hat{H}})} = \frac{e^{-\beta\hat{H}_1}}{Tr(e^{-\beta\hat{H}_1})} \frac{e^{-\beta\hat{H}_2}}{Tr(e^{-\beta\hat{H}_2})}$$

- The two density operators thus corresponds to the statistical operator of two systems which, if the interaction energy can be neglected, have no statistical correlations  $\Rightarrow$  the parameter  $\beta$  must be the same in the two subsystems and equal to the same parameter for the whole system.
- In everyday life, we have another way to express the same thing: we say that two bodies brought into thermal contact are in equilibrium if their temperatures are the same. This suggests that  $\beta$  must be related to the absolute temperature.
- Clearly, if initially we put all energy in the subsystem 2 (say), there will be energy transfer from subsystem 2 to subsystem 1 until thermal equilibrium is reached. From that moment on, no net energy flows from one subsystem to the other. When this equilibrium is reached, subsystem 1, say, has a density operator of the form

$$\hat{\rho}_1 = \frac{e^{-\beta\hat{H}_1}}{Tr(e^{-\beta\hat{H}_1})}$$

and the von Neumann entropy of the statistical mixture has its maximum value

31

31

- Furthermore,

$$S(\hat{\rho}) = -Tr\left[\hat{\rho}\ln\left(\frac{e^{-\beta\hat{H}}}{Z}\right)\right] = -Tr\left[\hat{\rho}\left(-\beta\hat{H} - \ln Z\right)\right] = \beta E + \ln Z$$

and this suggest that  $\beta$  should be proportional to the inverse of the temperature; in fact, in thermodynamics we have

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$$

- These are objective parameters, well known at the level of simple phenomenology of macroscopic systems; therefore, the theory of macro-systems in equilibrium which is coming out is nothing more than the well known thermodynamics. The connection is realized via the partition function

$$Q_N(V,T) = Z = Tr(e^{-\beta\hat{H}})$$

and the “thermodynamic” entropy  $S_B = k_B S(\hat{\rho}) = k_B \beta E + k_B \ln Z = E/T + k_B \ln Q_N(V,T)$

to obtain the Helmholtz free energy

$$F(N,V,T) = E - TS_B = -k_B T \ln Q_N(V,T)$$

32

32

## The grand canonical ensemble

- Consider now a statistical mixture representing the situation in which we know the average value of the total energy and of the number of particles, i.e. we make the following choice for the relevant observables:

$$\mathcal{M} = \{\hat{H}, \hat{N}\}$$

- This statistical mixture is called **grand canonical ensemble**, and the density operator which correspond to the maximum value of the von Neumann entropy is given by

$$\hat{\rho} = \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\mathcal{Z}} ; \quad \mathcal{Z} = \text{Tr}(e^{-\beta(\hat{H}-\mu\hat{N})})$$

- We try now to give a physical interpretation of the parameters  $\beta$  and  $\mu$ . As before, we consider a quantum system which consists of **two weakly interacting subsystems that can exchange energy and particles**. The density operator factorizes

$$\hat{\rho} = \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\text{Tr}(e^{-\beta(\hat{H}-\mu\hat{N})})} = \dots = \frac{e^{-\beta(\hat{H}_1-\mu\hat{N}_1)}}{\text{Tr}(e^{-\beta(\hat{H}_1-\mu\hat{N}_1)})} \frac{e^{-\beta(\hat{H}_2-\mu\hat{N}_2)}}{\text{Tr}(e^{-\beta(\hat{H}_2-\mu\hat{N}_2)})}$$

33

33

... and each factor can be considered as a density operator which describe a subsystem.

Once more, the parameters  $\beta$  and  $\mu$  must be equal in both subsystems and equal to the values in the whole system. Moreover at equilibrium the two subsystem reach the same temperature and the same chemical potential

We will assume that  $\mu$  is the **chemical potential** and  $\beta=1/k_B T$  as before. The grand canonical partition function is the normalization of the density operator:

$$\mathcal{Z} = \mathcal{Z}(\mu, V, T) = \text{Tr}(e^{-\beta(\hat{H}-\mu\hat{N})}) = \sum_{N=0}^{\infty} e^{\beta\mu N} \text{Tr}(e^{-\beta\hat{H}}) = \sum_{N=0}^{\infty} e^{\beta\mu N} Q_N(V, T)$$

- The thermodynamic entropy turns out to be

$$S = k_B S(\hat{\rho}) = -k_B \text{Tr} \left[ \hat{\rho} \ln \left( \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\mathcal{Z}} \right) \right] = -k_B \text{Tr} \left[ \hat{\rho} (-\beta\hat{H} + \beta\mu\hat{N} - \ln \mathcal{Z}) \right] = \frac{E - \mu N}{T} + k_B \ln \mathcal{Z}$$

and the connection with thermodynamics is completed via the **Grand potential**:

$$\Omega(\mu, V, T) = -k_B T \ln \mathcal{Z} = E - TS - \mu N$$

34

34

## The micro-canonical ensemble

- Consider now a different situation, in which we assume to know the total energy  $E$  of the quantum system. Of course, we cannot know this quantity with arbitrary precision
- We assume also that every state  $|n\rangle$  of the system with energy  $E \leq E_n \leq E + \Delta E$  has equal probability of being occupied, i.e.

$$\rho_i = \begin{cases} \text{cost.} & \text{if } E \leq E_i \leq E + \Delta E \\ 0 & \text{otherwise} \end{cases}$$

- From the normalization,  $\sum_i \rho_i = 1$ , it follows that  $\text{cost.} = \frac{1}{\Gamma(E, V, N)}$

being  $\Gamma(E, V, N)$  the number of states with energy  $E \leq E_n \leq E + \Delta E$  for a system with  $N$  particles in a volume  $V$

- The corresponding density operator is  $\hat{\rho} = \frac{1}{\Gamma(E, V, N)} \sum_n |n\rangle \langle n|$  and it is called **microcanonical**  
and the relative statistical mixture is called **microcanonical ensemble**

35

35

## Lecture 8: Suggested books

- L.E. Reichl "A modern course in Statistical Physics", Wiley
- R. K. Pathria, "Statistical mechanics", II ed., Oxford
- R.P. Feynman "Statistical Mechanics", The Benjamin/Cummings Publishing Company Ltd. (1982)
- W. Greiner, L. Neise, H. Stöcker "Thermodynamics and Statistical Mechanics", Springer (1997)

36

36

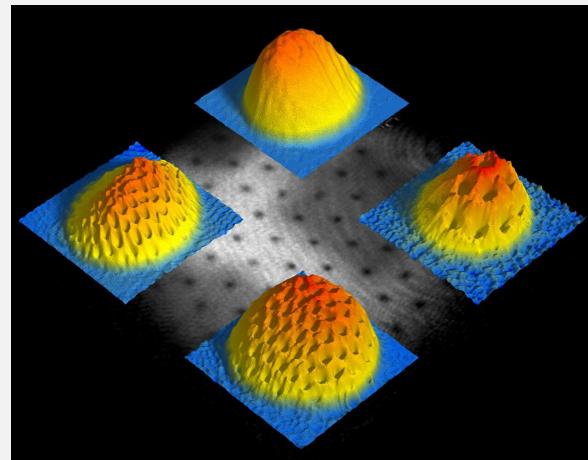


UNIVERSITÀ DEGLI STUDI DI MILANO

Advanced Statistical Physics

Lecture 8

Supplementary material



37



$T > T_\lambda$ : in the normal fluid phase,  
 $I_{\text{total}} = I_{\text{cylinder}} + I_{\text{helium}}$

liquid helium behaves as a normal fluid.  
 It will oscillate with the disk if  $d$  is smaller  
 than the viscous penetration depth ( $\delta$ )  $\delta = \sqrt{\frac{2\eta}{\rho\omega}}$

$\tau - \tau^* [\text{ns}]$

$T [\text{K}]$

Expected background

Superfluid Decoupling  $\Delta\tau$

Empty cell

Period shifted due to mass loading

$\tau = 2\pi\sqrt{\frac{I_{\text{cylinder}} + I_{\text{normal fluid}}}{K}}$

$T < T_\lambda$ : in the superfluid phase,  
 $\rho = \rho_n(T) + \rho_s(T)$

$I_{\text{total}} = I_{\text{cylinder}} + I_{\rho_n(T)}$

At  $T=0\text{K}$ ,  $\rho_n=0 \Rightarrow I_{\text{total}} = I_{\text{cylinder}}$

NCRI effects

Superfluid fraction:  
 at  $T=0\text{K}$  100% superfluid

$\rho_s/\rho_0$

$T [\text{K}]$

38

38