

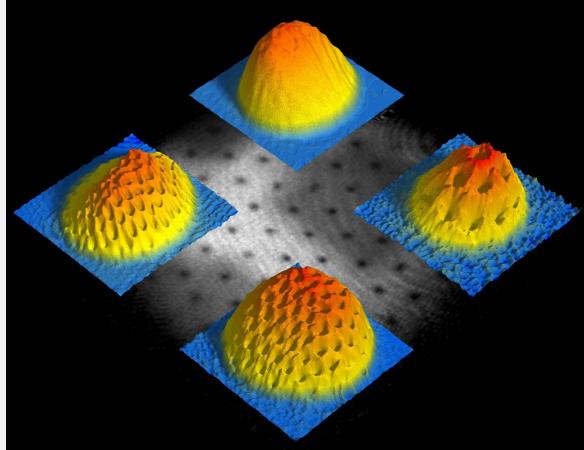


UNIVERSITÀ DEGLI STUDI DI MILANO

Advanced Statistical Physics

Lecture 2

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1



Outline

- Ideal gas
- Interacting systems
- Thermodynamic surfaces (ideal gas and real systems)
- Mean field approach
- Van der Walls equation of state
- The critical point
- Magnet-fluid analogy

Scope: to analyse the effect of interactions on a fluid with an approximate method (mean field approach) and discover that the interaction among constituents in the system can lead to emergent phenomena such as phase transitions and critical points; to investigate the analogies between magnetic systems and other complex systems as a first touch with universality in phase transitions

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2

2

The ideal gas in the canonical ensemble

- The advantage of using the canonical ens. becomes obvious when we are dealing with systems whose H decomposes into terms, each of which is a function of only one or a few degrees of freedom.
- In fact, while in the microcanonical ens., we must satisfy a constraint in which all the degrees of freedom appear, in the canonical ens., we can split our integrals into factors in which only few of them appear, and which can be evaluated explicitly.
- The ideal gas canonical partition function is \rightarrow *se lo calcoli per tutti*

*il microcanonico
è più difficile*

$$Q_N(V, T) = \int \frac{d^{3N} q d^{3N} p}{h^{3N} N!} e^{-\frac{1}{k_B T} \sum_{i=1}^{3N} p_i^2 / 2m} = \frac{V^N}{N!} \left[\int \frac{dp}{h} e^{-\frac{p^2}{2mk_B T}} \right]^{3N} = \dots$$

$$\dots = \frac{V^N}{N! \left(\sqrt{\frac{h^2}{2\pi m k_B T}} \right)^{3N}}$$

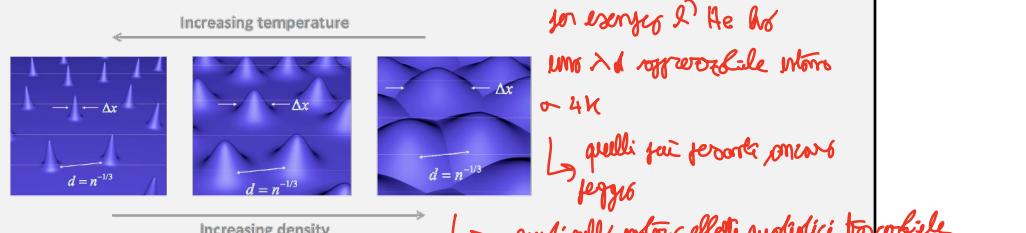
the quantity in brackets has the dimensions of length ...

3

3

Thermal de Broglie wavelength

- It is the *thermal de Broglie wavelength*
- $$\lambda_T = \sqrt{\frac{h^2}{2\pi m k_B T}}$$
- λ_T is roughly the average de Broglie wavelength of the particles in an ideal gas at the specified temperature T . \hookrightarrow *Sono i cieci che vedo la macchina*
 - We can take the average interparticle spacing in the gas to be approximately $(V/N)^{1/3}$ where V is the volume and N is the number of particles. When the thermal de Broglie wavelength is much smaller than the interparticle distance, the gas can be considered to behave classically.



- On the other hand, when the thermal de Broglie wavelength is on the order of or larger than the interparticle distance, quantum effects will dominate

4

4

per cui ragiono dissimilmente

2

By taking the logarithm (and using Stirling's formula ... $(x! \approx x^x e^{-x})$), we obtain the Helmholtz free energy

$$A(N,V,T) \approx -k_B T \ln \left[\left(\frac{eV}{N\lambda_T^3} \right)^N \right] = -Nk_B T \ln \left[\frac{eV}{N\lambda_T^3} \right]$$

by taking derivatives, we obtain the equations of state:

$$P = - \left(\frac{\partial A(N,V,T)}{\partial V} \right)_{N,T} = \frac{Nk_B T}{V}$$

penso come rispos
dell'energia libera a una
variazione di volume

$$S = - \left(\frac{\partial A(N,V,T)}{\partial T} \right)_{N,V} = Nk_B \ln \left(\frac{eV}{N\lambda_T^3} \right) - 3 \frac{Nk_B T}{T^{-1/2}} \frac{\partial}{\partial T} T^{-1/2} = Nk_B \ln \left(\frac{eV}{N\lambda_T^3} \right) + \frac{3Nk_B}{2}$$

From the definition $A=E-TS$ we obtain the value of internal energy

$$E = A + TS = -Nk_B T \ln \left(\frac{eV}{N\lambda_T^3} \right) + Nk_B T \ln \left(\frac{eV}{N\lambda_T^3} \right) + \frac{3Nk_B T}{2} = \frac{3Nk_B T}{2}$$

5

5

penso di dare oggi particolare lo stesso energie

→ come si scondenzano energie?

quindi chi interazione
non bende a zero

Equi-partition? *domanda di Goffi: come si è arrivati alla equipartizione se manca l'interazione? → forse ha sottratto l'argomento?*

- Note that we have just derived the equipartition theorem for an ideal mono-atomic gas:

$$\frac{E}{N} = \frac{\langle H \rangle}{N} = \frac{3}{2} k_B T$$

- each degree of freedom contributes to the average value of the energy with $1/2 k_B T$. But how can energy be equi-partitioned if the system is ideal: $H=\sum p_i^2/2m$, i.e. non interacting?
- Equipartition holds only for **ergodic** systems, i.e. for systems that are able to visit any microscopic state (q,p) with non zero probability: $p(q,p) \neq 0$. **This property is assumed in the ensemble theory** (for any particular ensemble), which thus models only ergodic systems!
- Strictly speaking, an ideal gas model isolated from the rest of the world (microcanonical ensemble) is not ergodic even when elastic scattering events are ad hoc introduced among particles. Another commonly cited counter-example where equipartition does not hold in the microcanonical ensemble is a system of coupled (and thus interacting) harmonic oscillators (see KAM theorem).
- Thus, do not think about the previously considered "ideal gas" as a model of a real ideal gas; it is simply a model useful to study the properties of a system where interactions can be overlooked

6

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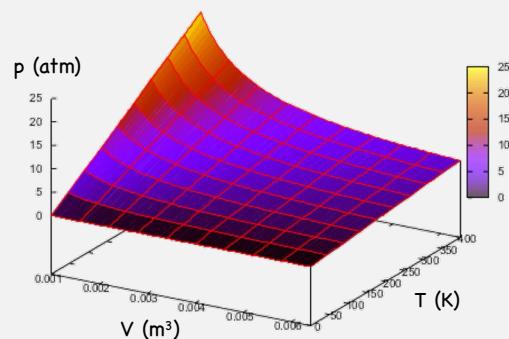
Equation of state

- Let's focus first on the **equation of state**, a functional relationship of the form $f(p, V, T) = 0$, which relates the thermodynamic parameters pressure p , volume V , and temperature T .
- The equation of state thus defines a **surface in a three-dimensional space** whose coordinates are P, V, T ; each of the points on this surface corresponds to an **equilibrium state of the system**. We will refer to this surface as the **thermodynamic surface**

For the classical **ideal gas** we obtained the following equation of state

$$p = \frac{Nk_B T}{V}$$

If we plot the relative thermodynamic surface in the (p, V, T) space for one mole of gas ($N \approx 6.022 \times 10^{23}$), we obtain the picture shown here

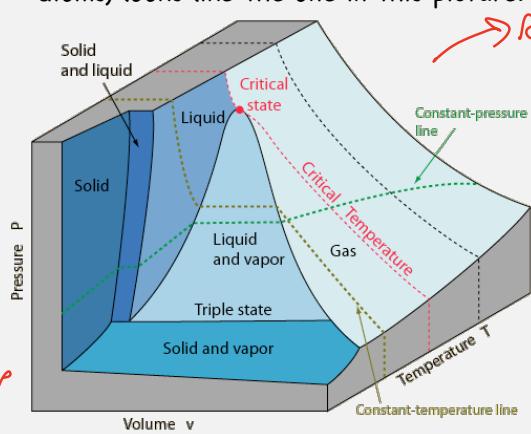


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7

Real thermodynamic surfaces

- The assumption of the absence of any interaction among particles implies the everlasting validity of this equation of state: we can have only a gas!
- Real substances do not have such a very simple thermodynamic surface; a typical thermodynamic surface of a **simple substance** (e.g. an assembly of not-too-light ideal gas atoms) looks like the one in this picture:



- The first thing that one should note is that different equilibrium states, which corresponds to values of the triplet (p, V, T) on this surface, represent **different phases of the same substance**: e.g. solid, liquid, gas
- Such phases can be found into well defined portions on the thermodynamic surface

8

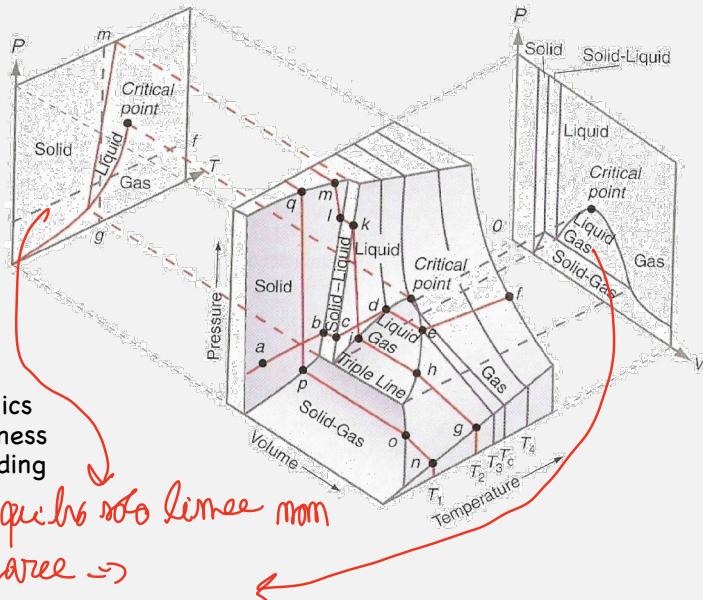
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quests cosa formalmente → riesce a trovare con lo f. statistico?

Phase diagrams

Phase diagrams are created by projecting the borders on the thermodynamic surface which delimit the different phases

- Can Statistical Mechanics reproduce all this richness of phenomena by including the interaction?



9

9

Interacting systems

- Previously we used the canonical statistical ensemble to study *classical* physical phenomena where, as a first approximation, it is possible to neglect the interactions among the degrees of freedom
- Now we want to investigate *classical* phenomena in which the **interaction** among the constituents play a role. In this case the **partition function** of the system **does not factorize** in contributes related to independent degrees of freedom; this makes the problem quite often intractable
- There are, however, situations where, as a first approximation, one can **recover a single particle treatment** by summarizing the effect of the inter-particle interactions with a "mean interaction potential" suffered by every particle. This is the **Mean field approach**, quite often very useful to catch the global aspects of a new phenomena
- The essential approximation in the mean field approach applied to a fluid is the **oversight of density fluctuations**: for a fluid in normal conditions this is not a problem but there are situations (critical point) where the system is dominated by fluctuations

10

10

Turning on the interaction

- The Hamiltonian of a fluid composed by N interacting identical particles posses the general expression:

$$H(q, p) = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + U(\vec{r}_1, \dots, \vec{r}_N) = H_0 + U(\vec{r}_1, \dots, \vec{r}_N)$$

Where H_0 is the ideal gas Hamiltonian and **U the many-body interaction** among the particles. Normally U is a function of the coordinates of the particles, but not of the momenta; let's go on with this assumption!

- The classical partition function of the canonical ensemble can be factorized as follows

fatto per quindici minuti.

$$Q_N(V, T) = \frac{1}{h^{3N} N!} \int d^N \vec{p} e^{-\frac{1}{k_B T} \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}} \int d^N \vec{r} e^{-\frac{1}{k_B T} U(\vec{r}_1, \dots, \vec{r}_N)} =$$

bo il gas ideale come fattore

$$= \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} \int d^N \vec{r} e^{-\frac{1}{k_B T} [U(\vec{r}_1, \dots, \vec{r}_N)]} = \frac{1}{N! \lambda_T^{3N}} \int d^N \vec{r} e^{-\frac{1}{k_B T} [U(\vec{r}_1, \dots, \vec{r}_N)]}$$

11

11

The configurational integral

- The **configurational integral or configurational partition function** Q_N^C , de facto characterizes the properties of the interacting system

$$Q_N^C(V, T) = \int d^N \vec{r} e^{-\frac{1}{k_B T} [U(\vec{r}_1, \dots, \vec{r}_N)]}$$

- When $U=0$, $Q_N^C=V^N$ recovering the ideal gas partition function
- When a model for the interaction is known, the calculation of Q_N^C normally represents an incredible task
- In many cases it is possible to use a model which tremendously simplify the task: one supposes that the **inter-particle interactions are pair additive**:

interazioni 2 corpi

$$U(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{2} \sum_{i \neq j=1}^N v(\vec{r}_i, \vec{r}_j) + \sum_{i,j,k=1}^N v^{(3)}(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots$$

12

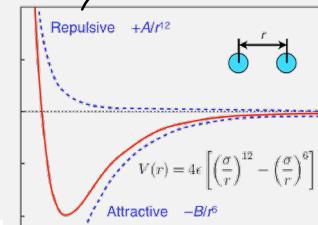
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non posso mettere leggi niente
per ad esempio niente

Pair interaction

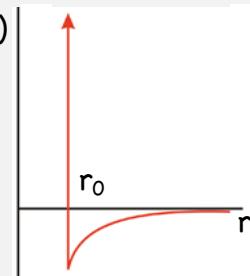
- This generally is not true, but can be a very good approximation, e.g. rare gas inter-atomic potential: short range repulsion and long ranges van der Waals attraction (dispersion forces). Even with this huge simplification our task is really arduous
- A typical pair interaction is the Lennard-Jones potential:

$$v(\vec{r}_i, \vec{r}_j) = v_{LJ}(|\vec{r}_i - \vec{r}_j|) = 4\epsilon \left[\left(\frac{\sigma}{|\vec{r}_i - \vec{r}_j|} \right)^{12} - \left(\frac{\sigma}{|\vec{r}_i - \vec{r}_j|} \right)^6 \right]$$



- In the following we will consider a pair interaction consisting of an hard-sphere term at short distance + an attractive term:

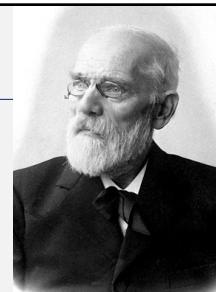
$$v(|\vec{r}_i - \vec{r}_j|) = \begin{cases} \infty & r < r_0 \\ -\epsilon e^{-(r-r_0)/\sigma} & r \geq r_0 \end{cases}$$



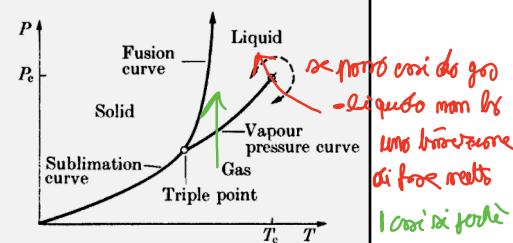
13

13

Van der Waals



- In 1873 Johannes Diderik van der Waals obtained the PhD title with a thesis entitled: "On the continuity of the liquid and gaseous states". The fundamental result of his work was an equation of state which foresees both the liquid and the gas phases, showing that these two states possess the same physical nature and can join in a continuous way.
- In other words, it exists a single fluid phase that only in certain thermodynamic conditions shows two distinct "faces"
- The method followed by van der Waals constitutes the prototype of the mean field approach and it is based on two points:
 - Each particle is treated as independent but subjected to an effective force which collects the average effect of the interactions with the other particles
 - Assume that the system is perfectly homogeneous: $\rho(r)=N/V=\text{const.}$



14

14

risposta alla questione di V. der Waals

Excluded volume

- Let's go back to the canonical partition function; assumption 1. corresponds to the following expression for the interaction:

$$U(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{2} \sum_{i=1}^N U_{\text{eff}}(\vec{r}_i)$$

offerto molto
 ↙ *Lo parte regalo lo mela*
come una confezione buona
non un modo ambiguo

- Assumption 2. allows for a strong simplification for U_{eff} : if the system is homogeneous, U_{eff} cannot depend on a particular position, thus $U_{\text{eff}} = \text{const.} = u_0$
- Moreover, two particles cannot approach each other indefinitely, a fraction of the total volume is not accessible for each single particle. *☒*
- With these two considerations we obtain:

$$Q_N(V, T) = \frac{1}{N! \lambda_T^{3N}} \int d^N \vec{r} e^{-\frac{1}{k_B T} [U(\vec{r}_1, \dots, \vec{r}_N)]} = \frac{1}{N! \lambda_T^{3N}} \left[\int_{V - V_{\text{exc}}} d\vec{r} e^{-\frac{u_0}{2k_B T}} \right]^N$$

$$\Rightarrow Q_N(V, T) = \frac{(V - V_{\text{exc}})^N e^{-\frac{Nu_0}{2k_B T}}}{N! \lambda_T^{3N}} = \frac{(V - bN)^N e^{-\frac{Nu_0}{2k_B T}}}{N! \lambda_T^{3N}} \quad \begin{array}{l} \text{volume escluso} \\ V_{\text{exc}} = bN \\ \hookrightarrow \text{dipende} \end{array}$$

del motore 6 unità di volume
non accessibile

15

Attractive forces

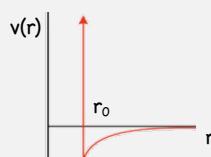
- In the last step we have assumed that the excluded volume should be proportional to the number of particles in the system: $V_{\text{exc}} = bN$
- The introduction of the excluded volume has an important consequence: the effective interaction potential u_0 is now defined as the average of the interactions with the other particles via the attractive part, $u_{\text{att}}(r)$, of the true pair interaction:

$$u_0 = 4\pi \int_{r_0}^{\infty} dr r^2 \rho(r) u_{\text{att}}(r) = \frac{4\pi N}{V} \int_{r_0}^{\infty} dr r^2 u_{\text{att}}(r)$$

Being r_0 the minimal distance reachable among two particles.

We finally obtain

$$a = -2\pi \int_{r_0}^{\infty} dr r^2 u_{\text{att}}(r) > 0 \quad \Rightarrow \quad u_0 = -2a \frac{N}{V}$$



- The constant a is positive given that in the previous integral only the attractive part is contributing. The parameters a and b characterize the specific fluid one is considering

i termini rettangolari
sono da V.W

16

16

- The canonical partition function turns out to be: $Q_N(V, T) = \frac{V^N}{N! \lambda_T^{3N}} \left[\left(1 - b \frac{N}{V}\right) e^{\frac{aN}{V k_B T}} \right]^N$

- The Helmholtz free energy is then obtained as $A = -k_B T \ln Q_N$:

$$A(N, V, T) = -k_B T \left\{ \ln \left[\frac{1}{N!} \left(\frac{V}{\lambda_T^3} \right)^N \right] + N \ln \left[\left(1 - b \frac{N}{V} \right) e^{\frac{aN}{V k_B T}} \right] \right\} =$$

Ideal gas

$$= -k_B T \left[\ln \left(\frac{1}{N! \lambda_T^{3N}} \right) + N \ln V + N \ln \left(1 - b \frac{N}{V} \right) + \frac{aN^2}{V k_B T} \right]$$

- The pressure is readily obtained:

$$P = - \left(\frac{\partial A(N, V, T)}{\partial V} \right)_{N, T} = k_B T N \left[\frac{1}{V} + \frac{1}{V^2} \frac{bN}{(1 - b\rho)} - \frac{1}{V^2} \frac{aN}{k_B T} \right] = \dots$$

17

17

The Van der Waals equation of state

And thus:

$$P = k_B T N \left[\frac{1}{V(1 - b\rho)} - \frac{1}{V^2} \frac{aN}{k_B T} \right] = \frac{k_B T \rho}{1 - b\rho} - a\rho^2$$

poche lenesce aumentano
 il contributo repulsivo
 la pressione maggiore

- We observe that in the first term the effect of the repulsive forces is to increase pressure respect to the ideal-gas value by reducing the effective available volume (in fact: $b\rho = bN/V = V_{\text{exc}}/V < 1$) **depende da b**
- The effect of attractive forces (second term) is to decrease pressure **per a**
- The effect of repulsive forces is proportional to the density ρ , whereas the effect of the attractive forces goes as ρ^2 , in fact the attractive interaction depends by the number of pairs in the system. We would expect, therefore, that at high ρ (not too much!) attractive forces will dominate
- We can write the van der Waals equation of state in the usual form:

$$\left[P + a \left(\frac{N}{V} \right)^2 \right] (V - bN) = N k_B T$$



18

18

Entropy of the Van der Waals fluid

- Starting from the Helmholtz free energy...

$$A(N, V, T) = A_0(N, V, T) - N \frac{aN}{V} - Nk_B T \ln\left(1 - b \frac{N}{V}\right)$$

- where A_0 is the free energy of the ideal gas, one can compute the entropy

$$S = -\left(\frac{\partial A(N, V, T)}{\partial T}\right)_{N, V} = S_0 + Nk_B \ln\left(1 - b \frac{N}{V}\right) < S_0$$

ci sono fermezze
nella molecola
↳ meno spazio

where S_0 is the entropy of the ideal gas.

- We observe that the entropy decreases respect to S_0 and this effect is due to repulsive forces only
- This is in agreement with the interpretation of the entropy as a function of the accessible "volume" in the phase space: only the excluded volume reduces this region

19

19

Compressibility of the Van der Waals fluid

- Let's go back to the van der Waals eq. of state: $p = \frac{k_B T \rho}{1 - b\rho} - a\rho^2$
- Only the first term depends on the temperature. For large T, the first term dominates and the behavior becomes similar to an ideal gas
- At low T it is instructive to consider the isothermal compressibility: $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{N, T}$

- We have

$$\frac{\partial p}{\partial V} = \frac{\partial}{\partial V} \left(\frac{k_B TN}{V - bN} - a \frac{N^2}{V^2} \right) = -\frac{k_B TN}{(V - bN)^2} + 2a \frac{N^2}{V^3}$$

liquido ↗ molle giusto
gas ↘ inconfondibile

- For $V \approx bN$ the compressibility turns out to be very small (and pressure very high), whereas for $V \gg bN$ compressibility is very high (and pressure very low). Such behaviors are those we usually ascribe to a liquid and a gas respectively

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20

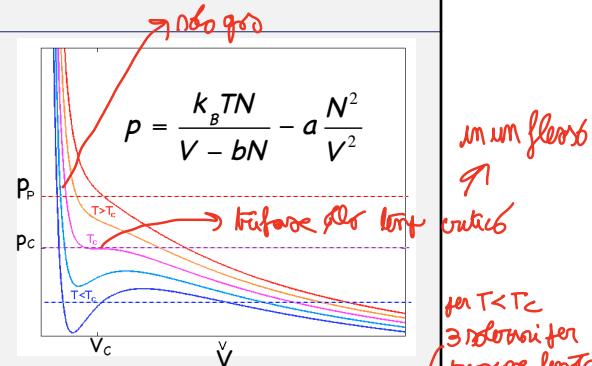
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The critical point

- The van der Waals pressure p at fixed T (isotherms) as a function of the volume $p=p(V)$, is represented by a series of curves like those in this picture
- From the eq. of state we can obtain a cubic polynomial in V :

$$(V - bN)(pV^2 + aN^2) = k_B TN V^2$$

$$pV^3 - (bNp + k_B TN) \cdot V^2 + aN^2 \cdot V - bN^3 = 0$$



- For a given pressure, there is a temperature range in which the polynomial has three real roots...
- As we increase T these roots closer together, and merge at $T=T_c$, the critical point.
- For $T > T_c$ one real root remain.

21

21

The critical point

- We will call critical volume, V_c , and critical pressure, p_c , the point where first and second derivative of pressure goes to zero. We can find the critical point parameters p_c , V_c , T_c as follows...

$$\begin{cases} \frac{\partial p}{\partial V} \Big|_{V_c} = -\frac{Nk_B T_c}{(V_c - bN)^2} + 2a \frac{N^2}{V_c^3} = 0 \\ \frac{\partial^2 p}{\partial V^2} \Big|_{V_c} = \frac{2Nk_B T_c}{(V_c - bN)^3} - 6a \frac{N^2}{V_c^4} = 0 \end{cases}$$

From the 1st eq.

$$T_c = 2a \frac{N(V_c - bN)^2}{k_B V_c^3}$$

Substituting into the 1st eq.

$$\Rightarrow T_c = 2a \frac{(2b)^2}{k_B (3b)^3} = \frac{8}{27} \frac{a}{k_B b}$$

Substituting in the 2nd eq. $\frac{2}{(V_c - bN)} - \frac{3}{V_c} = 0 \Rightarrow V_c = 3bN$

Substituting into the eq. of state:

$$p_c = \frac{1}{2b} \frac{8a}{27b} - \frac{a}{9b^2} = \frac{a}{27b^2}$$

22

22



"Corresponding" critical point

- Note that three quantities T_c , p_c and V_c have been expressed in terms of only two parameters, namely, a and b .

$$V_c = 3bN \quad T_c = 8a/27bk_B \quad p_c = a/27b^2$$
- Therefore, there must be one relation involving T_c , p_c and V_c which is independent of the parameters a and b .
 Clearly,
$$R = \frac{P_c V_c}{Nk_B T_c} = \frac{3}{8} \rightarrow \text{quoziente di universo}$$

$$\rightarrow \text{per tutte le sostanze}$$
- in contrast to the relation $R=pV/(Nk_B T) = 1$ for all P,V,T in the case of the ideal gas.
 Experiments gives $R \approx 3/10$ \rightarrow c'è universo ma con un fattore diverso
- This is a first manifestation of the law of corresponding states, that we are going to discuss later on \star
- Note that the specific values of the T_c , p_c and V_c of various different fluids depend on the corresponding specific values of the parameters a and b which are, in turn, determined by their corresponding microscopic details of the inter-molecular interactions

23

23

Instability of density fluctuations

- Below T_c , in the region where pressure increases we have

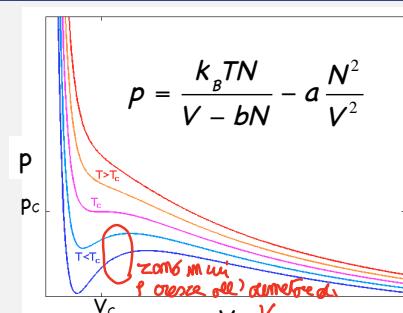
$$\frac{\partial p}{\partial \rho} = \frac{\partial p}{\partial V} \frac{\partial V}{\partial \rho} = -\frac{N}{\rho^2} \frac{\partial p}{\partial V} < 0$$

i.e., in this region, p decreases with density

- Consider now a spontaneous density fluctuations in the system in a state at $T < T_c$ with a volume in this region: there will be a portion of the volume, δV , at density higher than the average density ρ ; pressure will be lower in δV and thus for the effect of the pressure in the surrounding regions, particles in δV will tend to collapse. Conversely, low density region will tend to expand, being at higher pressures

- Thus, negative compressibility $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{N,T}$

gives rise to instable regions where the fluid tends to separate in regions at high and low densities: phase separation



dove ha un punto di minimo ha un incremento di pressione \Rightarrow più la zona instabile offre una forza più forte

24

Almeno se P

quegli $\frac{\partial p}{\partial \rho} > 0$ è vero
condizione fuori dall'equilibrio

portano allo instabile \leq collasso
di liquido-gas per non uniforme

12

Free energy and phase coexistence

per avere
stabilità
quindi $A(V)$ convessa

- The stability condition for the compressibility implies that $\frac{\partial^2 A}{\partial V^2} = -\frac{\partial p}{\partial V} > 0$
 which means that the Helmholtz free energy should be convex (or concave upward)
- We know that at equilibrium $A(N,V,T)$ is minimal. Therefore, to see if the fluid will separate in two phases we should compare the free energy of the single-phase system with that, A_2 , of the double-phase one
- We will call $A_a/N, V_a/N$ the free energy per particle and volume per particle of the single homogeneous phase of type (a) which consists of all N particles, and $A_b/N, V_b/N$ the corresponding values for the single homogeneous phase of type (b) which consists of all N particles. Due to extensivity of A the free energy of the double-phase system, A_2 , is

$$A_2 = N_a \frac{A_a}{N} + N_b \frac{A_b}{N} \quad \text{ipotesi 2 fasi a e b}$$

25

25

Free energy and phase coexistence

- Moreover, it should be that $V = N_a \frac{V_a}{N} + N_b \frac{V_b}{N}$
 $\Rightarrow \frac{N_a}{N} = \frac{V - V_b}{V_a - V_b}; \frac{N_b}{N} = \frac{V - V_a}{V_b - V_a} \Rightarrow A_2 = \frac{V - V_b}{V_a - V_b} A_a - \frac{V - V_a}{V_a - V_b} A_b$

- Therefore

$$A_2 = A_a + \frac{V - V_a}{V_b - V_a} (A_b - A_a)$$

i.e. a straight line which connects the two points on $A(V)$ where the system is completely in phase (a) and (b)

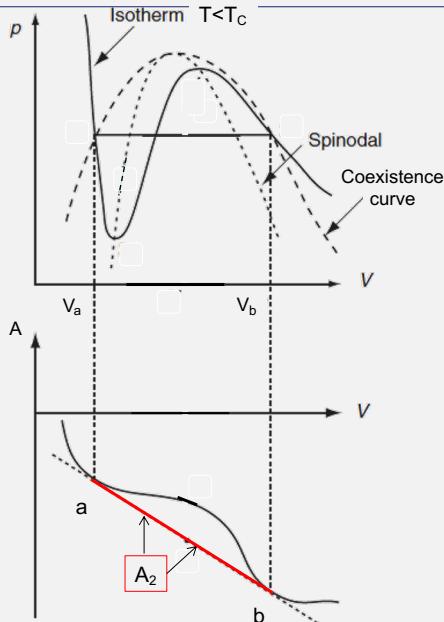
- When $T > T_c$ the system is stable and $A(V)$ is convex (concave upward), thus the straight line lies always above $A \Rightarrow A_2 > A(V)$
- When $T < T_c$ there is a region where $A(V)$ is concave downward \Rightarrow one can always find two points such that the whole straight line, connecting them, will lie below $A \Rightarrow A_2 < A(V)$

\hookrightarrow le 2 fasi non si incontrano

26

26

Coexistence & spinodal curves



For volumes between V_a and V_b the Helmholtz free energy of the double-phase system is below the one of the monophasic system and will constitute the thermodynamic equilibrium of the system

inside $[V_a, V_b]$, being $A(V)$ a straight line, the corresponding pressure, $p = -\partial A / \partial V$, would be a constant

- We can repeat this analysis for every $T < T_c$ obtainin the **coexistence curve**
- We note that this region is larger than the region of **thermodynamic instability** ($\partial p / \partial V > 0$); by joining the points which border the instability region one obtains the **spinodal curve**, which lies inside the coexistence curve

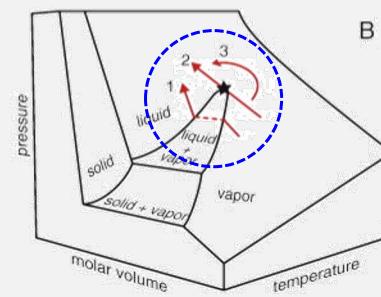
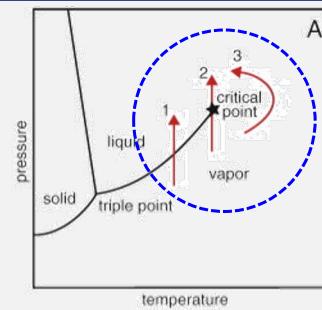
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27

The liquid-gas transition

- By studying the van der Waals fluid (mean field approach) we have been able to understand qualitatively the **thermodynamic surface** near the **critical point** and the **gas-liquid coexistence curve**:

1. For $T < T_c$ and $p < p_c$ the transformation from gas to liquid happens rapidly via condensation (boiling: liquid \rightarrow gas)...
2. At T_c and/or p_c the situation change...
3. And circling the critical point with $T > T_c$ and $p > p_c$ one can go continuously from the liquid to the gas phases via a thermodynamic path above the critical point without any discontinuity



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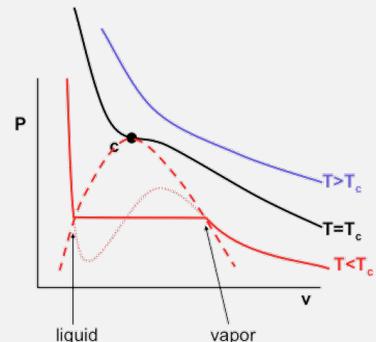
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The critical point

- Now we analyse what happens when, being in an homogeneous phase, we approach the critical point
- Near the critical point we have

$$\frac{\partial P}{\partial V} \rightarrow 0$$

and therefore $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{N,T} \rightarrow \infty$



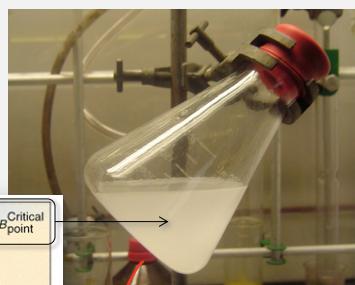
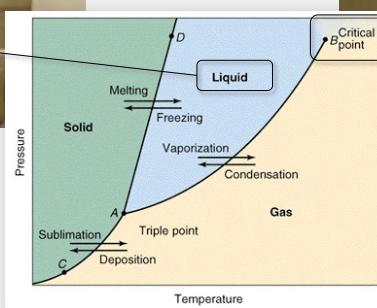
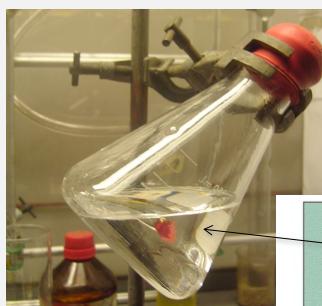
- This means that spontaneous density fluctuations (remember the discussion on the equivalence of canonical and grand canonical ensembles in the previous lecture) diverge by approaching the critical point: in the fluid, at each instant, more and more extended regions are created, in which the density is higher or lower than average.
- It is as if the system, despite being in the region monophasic, prepare to phase separation, creating spontaneously regions similar to the gas or liquid.

29

29

The critical opalescence

- This phenomenon has considerable visual effects: in the presence of density fluctuations, a fluid diffuses in all directions, part of the light from which is invested; near the critical point a fluid becomes turbid, whitish, is the phenomenon of critical opalescence.



U sono simili di qualche
modo/lunghezza d'onda
Luce oscurata

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The law of corresponding states

- Now we want to investigate how thermodynamic properties behave near the critical point. Let's go back to the van der Waals equation of state

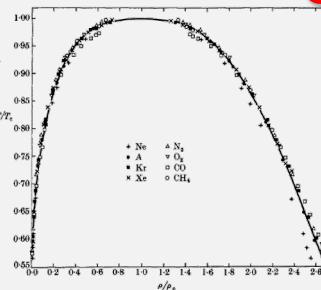
$$\left[p + a \left(\frac{N}{V} \right)^2 \right] (V - bN) = N k_B T \quad \begin{cases} V_c = 3bN \\ T_c = 8a/27bk_B \\ P_c = a/27b^2 \end{cases} \quad \left(R = \frac{P_c V_c}{N k_B T_c} = \frac{3}{8} \right)$$

- One can introduce new rescaled variables: $\tilde{T} = \frac{T}{T_c}$; $\tilde{V} = \frac{V}{V_c}$; $\tilde{P} = \frac{P}{P_c}$

and the eq. of state can be rewritten in an universal form:

$$\left[\tilde{P} + \frac{3}{\tilde{V}^2} \right] (3\tilde{V} - 1) = 8\tilde{T}$$

- This equation does not contain any constant characteristic of the substance. If the Van der Waals hypothesis were correct, would hold for all substances. This is the **law of corresponding states**. Experimental data, properly normalized, fall on one and the same curve: qualitative accord with this law



31

31

Magnets

- In general, three main types of magnetism are distinguished: **diamagnetism, paramagnetism, and ferromagnetism**.
- Paramagnetism** is a form of magnetism whereby certain materials form internal induced magnetic fields in the direction of the applied magnetic field and are attracted by an externally applied magnetic field. In contrast, **diamagnetic materials** form induced magnetic fields in the direction opposite to that of the applied magnetic field and are repelled by magnetic fields.
- There are also several **spontaneous** magnetic states (without an externally applied magnetic field): **ferromagnetism** and **antiferromagnetism** are the two most important; a state in which all the magnetic moments are aligned in the same direction corresponds to ferromagnetism, if aligned in antiparallel directions, with zero resulting macroscopic magnetization is zero, is antiferromagnetism .
- Can we understand ferromagnetism in terms of electron currents in the framework of Maxwellian classical electrodynamics and classical statistical mechanics?

32

32

The Bohr-van Leeuwen theorem

*nogoms parone il magnetismo
com le m. sferzate classico quindi senza spin*

- Neglecting "classical" spin (as spin, an intrinsic angular momentum, is really a quantum concept itself), spontaneous magnetism is associated with circulating currents. Thus, one may ask whether a magnetic moment:

$$\langle M \rangle = \left\langle \sum_i q_i \vec{v}_i \times \vec{r}_i \right\rangle$$

can exist, where expectations are with respect to classical statistical mechanical distributions

- For N classical charged particles with positions \mathbf{r}_i and moments \mathbf{p}_i , the partition function is

$$Q_N(V, T) = \int \prod_i d\vec{r}_i d\vec{p}_i \exp\left(-\frac{H}{k_B T}\right)$$

where H is the classical Hamiltonian function

$$H = \sum_i \frac{[\vec{p}_i + q_i \vec{A}(\vec{r}_i)]^2}{2m_i} + V(\vec{r}_1, \dots, \vec{r}_N)$$

- \mathbf{A} is the vector potential related to the magnetic induction \mathbf{B} through $\mathbf{B} = \nabla \times \mathbf{A}$. The only assumption made are that \mathbf{B} is only due to the currents (No external magnetic field), and all the interactions between particles depend only on their positions, and not velocities.

33

33

- For each particle the components of the position \mathbf{r}_i and moment \mathbf{p}_i , are related by the equations of Hamiltonian mechanics:

$$\dot{\vec{r}}_i = \frac{\partial H}{\partial \vec{p}_i} \quad \dot{\vec{p}}_i = -\frac{\partial H}{\partial \vec{r}_i}$$

therefore: $\dot{\vec{r}}_i = \vec{v}_i \propto \vec{p}_i + q_i \vec{A}(\vec{r}_i)$

so the magnetic moment $\langle M \rangle$ is a linear function of the momenta \mathbf{p}_i

- The thermally averaged magnetic moment

$$\langle M \rangle = \int \prod_i d\vec{r}_i d\vec{p}_i M \exp\left(-\frac{1}{k_B T} H\right),$$

as evident by a change of variable $\mathbf{p}_i \rightarrow \mathbf{v}_i$, is the sum of terms proportional to integrals of the form

$$\int \prod_i d\vec{r}_i d\vec{v}_i \vec{v}_i \exp\left(-\frac{1}{k_B T} H\right)$$

- The integrand is an odd function of \mathbf{v}_i , so it vanishes. Spontaneous magnetization is a quantum effect! The next guess might be that one should consider atomic moments arising from electronic spins and electronic orbital motion, and then consider the magnetostatic interaction between them.

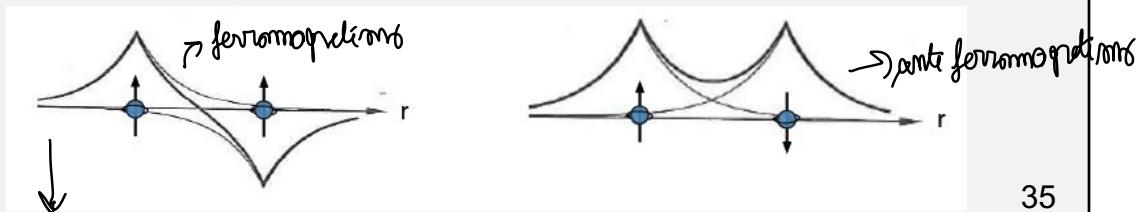
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34

Quantum Exchange

\rightarrow dentro il termine di Romesh man parla
i magneti a T zero \Rightarrow nostra allora solo a T=0 \rightarrow da qui l'idea di un
termine che
"magnetizza"

- It turns out that the contribution of magnetostatic interactions to alignment between dipoles is not only insufficient, but is also negligible compared to the real source of interactions: exchange interactions
- Exchange interactions are related to the **connection between symmetry of spin and spatial wavefunctions for electrons as fermions**, and so the energy scales associated with these interactions are associated with the energy scales of the spatial degrees of freedom; i.e. electronic kinetic energy and Coulomb interaction
- In fact, a given spin configuration restricts the range of possible spatial configurations, and because different spatial configurations can have significantly different energies, there is thus a large energy associated with different spin configurations.



35

35

\rightarrow i punti repulsivi devono in buona parte sovrapporsi

\rightarrow se punti repulsivi non si sovrappongono, e vicino \Rightarrow così ci sono un certo numero

di contatti

There are two main types of exchange interactions:

- **Direct exchange** - This is driven by minimising potential energy, by reducing wavefunction overlap. Wavefunction overlap is reduced by adding nodes to the wavefunction, producing antisymmetric spatial many-body wavefunctions, and so favours symmetric spins, i.e. ferromagnetic interactions. This case generally arises when electrons occupy wavefunctions that overlap in space.
- **Kinetic exchange** - This is driven by minimising kinetic energy, by reducing gradients of wavefunctions, i.e. allowing delocalisation of electrons. This corresponds to using symmetric superpositions of wavefunctions, and so favours antisymmetric spins, i.e. antiferromagnetic interactions. This case generally arises for localised electronic orbitals
- The **many-body equilibrium state** which manifests **spontaneous magnetization** is obtained as a subtle and not trivial combination of these and other competing effects (see cap.4 in "Theory of Magnetism" on Ariel)
- The form of the **exchange interaction among 2 spins is typically**: $E_{12} = -J_{12} \vec{S}_1 \cdot \vec{S}_2$ with $J>0$ for the ferromagnetic case and $J<0$ for the antiferromagnetic case

36

36

Different types of magnetism & magnetic behaviours

"faster outside"



H magnetic field,
(p pressure,
 T temperature,
 μ chemical pot.,
 E electric field)
≡
generalized
force

type	spin alignment	spin in simplified plot	examples
ferromagnetic	all spins align parallel to one another: spontaneous magnetization - $M = a + b$		Fe, Co, Ni, Gd, Dy, Sm ₂ O ₃ , Sm ₂ Co ₁₇ , Nd ₂ Fe ₁₄ B
ferrimagnetic	most spins parallel to one another, some spins antiparallel: spontaneous magnetization - $M = a - b > 0$		magnetite (Fe ₃ O ₄), yttrium iron garnet (YIG), GdCo ₅
antiferromagnetic	periodic parallel-antiparallel spin distribution: $M = a - b = 0$		chromium, FeMn, NiO
paramagnetic	spins tend to align parallel to an external magnetic field: $M = 0 @ H=0, M \neq 0 @ H \neq 0$		oxygen, sodium, aluminum, calcium, uranium
diamagnetic	spins tend to align antiparallel to an external magnetic field $M = 0 @ H=0, M \neq 0 @ H > 0$		superconductors, nitrogen, copper, silver, gold, water, organic compounds

"magnetic field
rotation"



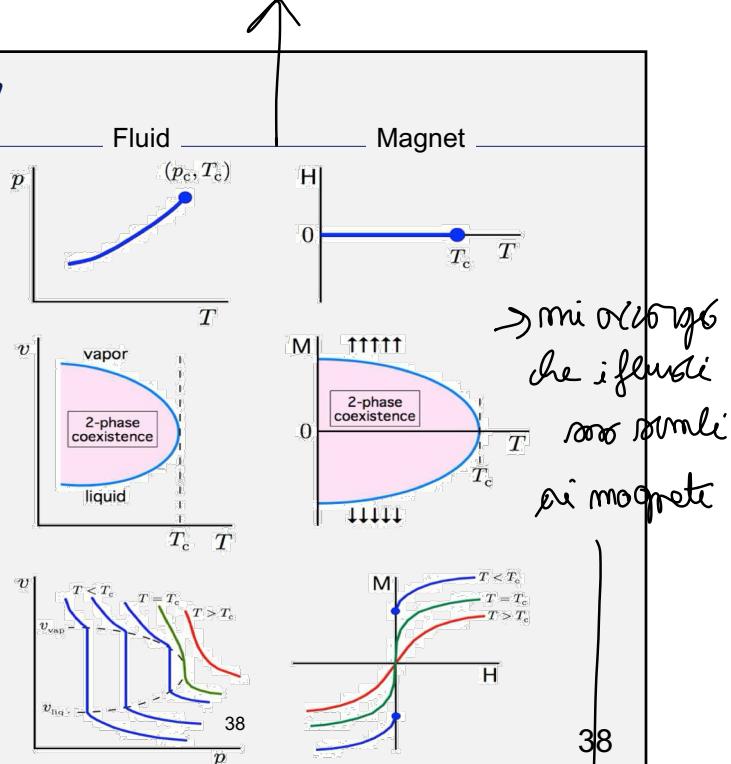
M magnetization,
(V volume,
 S entropy,
 N # of particles,
 P polarization)
≡
generalized
displacement

37

generalmente i dati sperimentali

Fluid-Magnet analogy

- In the thermodynamic paradigm of **generalized forces** and **generalized displacements**, the **magnetic field** H and **magnetization** M corresponds to pressure p and volume V , respectively, for a fluid
- The equilibrium phases of a **ferromagnetic system** on the **H-T diagram**, the two-phase coexistence region on the corresponding **M-T diagram** and the isotherms on the **M-H diagram** are shown schematically here...
- where the analogous diagrams for a typical simple fluid are also plotted to emphasize the **deep analogy** between these two types of systems ... a **more deep example of Universality!**

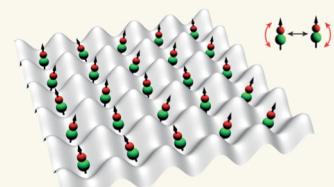


37

coincide molto bene
dove si uniscono

Spin models

- What is at the origin of the magnetic-fluid analogy?
- A number of physical/chemical systems which undergo phase transitions can be represented, to varying degrees of accuracy, by an "array of lattice sites, with (sometimes only nearest-neighbor) interaction that depends upon the manner of occupation of the neighboring sites"
- This simple-minded model turns out to be good enough to provide a unified, theoretical basis for understanding a variety of phenomena such as ferromagnetism and antiferromagnetism, gas-liquid and liquid-solid transitions, order-disorder transitions in alloys, phase separation in binary solutions, etc (see supplementary material!).
- There is no doubt that this model considerably oversimplifies the actual physical systems it is supposed to represent; nevertheless, it does retain the essential physical features of the problem-features that account for the propagation of order, from the microscopic to the macroscopic scale in the system. Accordingly, it does lead to the onset of a phase transition in the given system, which arises as a cooperative phenomenon.



Synthetic quantum spin system:
confined ultracold molecules
Nature 501, 497 (2013)

Lecture 2: Suggested books

- L. Peliti, "Appunti di meccanica statistica", Bollati Boringhieri
- R. Piazza "Note di Fisica Statistica" Springer
- R. K. Pathria, "Statistical mechanics", II ed., Oxford

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Advanced Statistical Physics

Lecture 3

Supplementary material

41

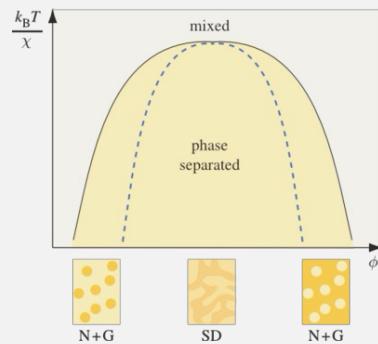
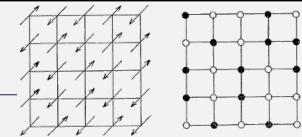
The lattice gas

- The Ising model could apply equally well to a "lattice gas" i.e. a collection of atoms which can occupy only discrete positions in space that constitute a lattice structure with a given number of nearest neighbours (Yang and Lee, 1952)
- Each lattice site can be occupied by at most one atom, and the interaction energy between two occupied sites is nonzero, say $-\varepsilon$, only if the sites involved constitute a nearest-neighbor pair.
- The configurational energy of the gas is then given by $E = -\varepsilon n$, where n is the total number of nearest-neighbor pairs (of occupied sites) in a given configuration of the system. Clearly N , the number of lattice sites, here plays the role of the "total volume" available to the gas.
- Case $\varepsilon > 0$: attractive interaction possible model for a gas-liquid transition
- Case $\varepsilon < 0$: repulsive interaction, configurations with alternating sites being "occupied" and "unoccupied" are the more favored ones, model of solidification

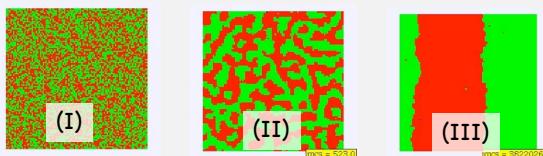
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Binary alloy & spinodal decomposition

- In a **binary alloy** we have a lattice structure consisting of **two types of atoms**
- In a configuration characterized by the numbers N_{11} , N_{22} and N_{12} of the three types of nearest-neighbor pairs, the configurational energy of the alloy may be written as $E = (\epsilon_{11} N_{11} + \epsilon_{22} N_{22} + \epsilon_{12} N_{12})$, where ϵ_{ij} , has the obvious meaning of an interaction energy among type i and j
- The following is a (Monte Carlo) simulation of a **spinodal decomposition** in a binary alloy at a temperature $T < T_C$ in the phase separation region (**2D ferromagnetic, $J > 0$, Ising model where N_1 and N_2 is conserved**); it started from a disordered configuration (I) and reached phase separation at longer "times" (II & III)



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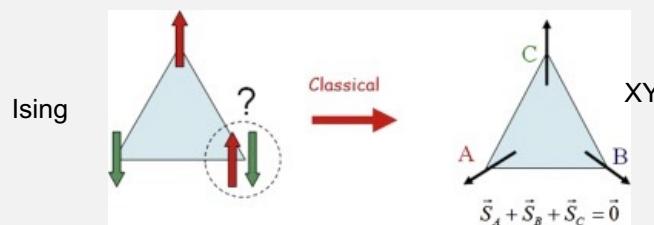
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43

Frustration and spin models

The key question for a spin system is to determine the **ground state**. For **ferromagnetic** couplings, the ground state is simple: all spin pointing in the same directions (a ferromagnetic state, if present!).

For **anti-ferromagnetic** couplings, it depends on **geometry**. For example, on a square lattice, the spins can find a way to make all spins happy (all neighboring spins stay in opposite directions). But on a triangular lattice, there is no way to make all the spin happy in an Ising model with $J < 0$. So the spins are "frustrated". This type of systems are known as **frustrated magnets**.



The reason that frustrated magnets are interesting is because their **ground states are not obvious**. Therefore, some of these system may have very strange ground state, with exotic properties, such as spin

44

44

Spin glasses

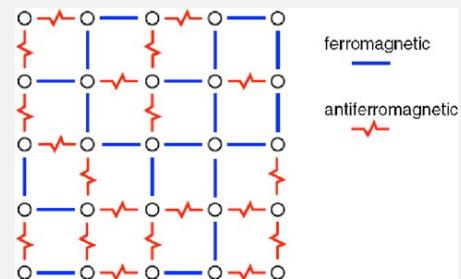
- A **spin glass** is a **disordered magnet**, where the magnetic spins are not aligned in a regular pattern. The term "glass" comes from an **analogy** between the magnetic disorder in a spin glass and the positional disorder of a conventional, **chemical glass**.

A spin glass is always frustrated; its Hamiltonian is typically of the form:

$$H = -\frac{1}{2} \sum_{i,j} J_{ij} \sigma_i \sigma_j$$

where $J_{ij} = \pm 1$ randomly.

- The **range of each interaction** can be potentially **infinite** (of the order of the size of the lattice) and this is the **Sherrington-Kirkpatrick** (mean-field spin-glass approximation) model.
- When **interaction** is considered only among **nearest neighbor** we have the **Edwards-Anderson** model.
- Finding the ground state (minimum energy state) of a generic **Ising** model is **NP-hard** (Barahona, 1982). So, maybe we can map hard problems on an Ising model.



45

45

More spin models applications

46

- There are also **application outside Physics**, for example **biology** where spins (**up=1**, **down=0**) have been used to represent the activity of **network of neurons**, but also **flocking birds**, or **beating heart cells** ... etc.
- But there is also a long tradition of using spin models to represent **social interactions** and **organization**. Indeed, the analogy between magnetic polarization and opinion polarization was presented in the early 1970s, in the framework of "Socio-dynamics". In the following decade, several efforts towards a quantitative sociology developed based on models essentially undistinguishable from spin models.
- Also a large set of **economic/financial models** can be mapped onto various versions of spin models to account for **social influence in individual decisions**. The Ising model is indeed one of the simplest models describing the **competition between the ordering force of imitation or contagion and the disordering impact of private information or idiosyncratic noise**



46

23

Even more than “models”

Spin models can also turn out to become a useful **computational tool** or a **new computational paradigm**

Consider a particular **spin configuration** of an **Ising model**; given such a configuration, like any other, we can think about it as the **ground state of specific class of** (presently unknown/unexpressed) **Hamiltonians**

- We can also associate a 1 to each up spin and a zero to each down spin
- From the point of view of information theory, considering spin as a **binary alphabet**, the given configuration could represent everything, from a number to one or more phrases.
- If this number (or anything else) is the **solution** of a problem we can try to solve our problem in two steps:
 1. Solve an **embedding problem**, i.e. find one Hamiltonian for which this configuration is a ground state (not necessarily an easy task!)
 2. **Annealing**: let your spin model to **evolve toward its ground state** (for example reducing its “temperature”) and ... read the solution!

In principle, the model could be **physically implemented, not only simulated**.

47

1	0	1	0	0	1	0	0	1
0	0	1	0	1	0	1	0	1
0	0	0	0	0	0	1	1	1
1	0	0	1	0	0	0	0	0
1	1	0	0	1	0	0	1	0
1	1	1	0	0	1	1	0	0
0	0	1	0	1	0	1	1	0
1	0	0	1	1	1	1	1	1
0	0	0	1	1	1	0	0	0