Interactions

Reference books:

- **Quantum mechanics:**
  - Mathews: Introduction to Quantum Mechanics
  - Cohen-Tannoudji, Diu and Laloë: Mécanique Quantique
- **Statistical physics:**
  - Reif (Berkeley lecture): Statistical and Thermal Physics
  - Diu, Guthmann, Lederer, Roulet: Physique statistique
- **Phase transition:**
  - Landau and Lifchitz: Statistical Physics
  - Boccara: Symétries Brisées (“Broken Symmetry”)
- **Solids state physics:**
  - Kittel: Introduction to solid state Physics,
  - Ashcroft and Mermin: solid state Physics,
  - Feng Jin: introduction to Condensed Matter Physics

Interactions

- Phase Transformations:
  - atoms or molecules interact with each-other: **COOPERATIVITY**

    $$H_{total} \neq \sum_i H_i$$

  - complex situations can occur
  - recent understanding (Van der Waals XIXth century, Williams' Nobel price in 1982)

- Thermal motion destroy disorder:
  - interactions which are responsible for phase transitions may not be cancelled by thermal motion under critical temperature T_c !

Effective interactions ~ $k_B T_c$

Interactions

- Phase Transformation :
  - "HT" stable phase above T_c is more disordered ("high symmetry")
  - "LT" stable phase below T_c is more ordered ("low symmetry")
  - free enthalpy **at T_c**

$$\left.\begin{array}{l}\Delta G = G_{LT} - G_{HT} = 0 \\ \Delta G = \Delta(H - TS) = 0\end{array}\right\} \quad \Delta H = T_c \Delta S$$

  - increasing order when going from "high" to "low" symmetry phase:

$$\Delta S = k_B \ln(\Omega_{LT}/\Omega_{HT}) \approx k_B$$

$$\Delta G(T=0K) \sim \Delta H(T_c) \sim T_c\, \Delta S(T_c) \sim k_B T_c$$

Interactions

• All interactions leading to phase transition have electronic origin:

– which ones can be of the order of $k_B T_c$ in the range one usually finds or would like to find the phase transitions to occur ($k_B T_c$< few tens of meV) ?

• **Point charge interaction ?**

$$U \approx \frac{1}{4\pi\varepsilon_o}\frac{e^2}{r}$$

$\varepsilon_o \sim 8.8\ 10^{-12}$
$e \sim 1.6\ 10^{-19}$
$r \sim 3\ 10^{-10}$

U ~ 7.7 10-19 J ~ 4.8eV >> kBTc !!!

Interactions

- **Dipolar interaction ?**

P = q·d
q ~ e
d ~ 3 10^{-10}

p ~ 5 10^{-29} C ·m ~ 15 Debye
(Water: 1.84 Debye)

Electric field generated by a dipole $$\vec{E} = \frac{1}{4\pi\varepsilon_0} \frac{3(\vec{p}\cdot\vec{r})\vec{r} - r^2\vec{p}}{r^5}$$

$1/r^3$ decreases more rapidly than $1/r^2$ (point charge)

$$\vec{p} \perp \vec{r} \qquad E = \frac{1}{4\pi\varepsilon_0} \frac{2p}{r^3}$$

$$\vec{p} // \vec{r} \qquad E = \frac{-1}{4\pi\varepsilon_0} \frac{1p}{r^3}$$

Two dipoles interaction energy

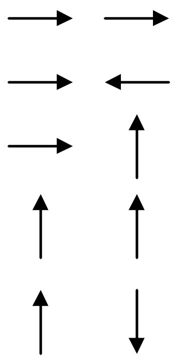
$$U = -\vec{p}_2 \cdot \vec{E}(\vec{p}_1) = \frac{-1}{4\pi\varepsilon_0} \frac{3(\vec{p}_1\cdot\vec{r})(\vec{p}_2\cdot\vec{r}) - r^2(\vec{p}_1\cdot\vec{p}_2)}{r^5}$$

Interactions

- **Dipolar interaction :**

$$U = -\vec{p}_2 \cdot \vec{E}(\vec{p}_1) = \frac{-1}{4\pi\varepsilon_o} \frac{3(\vec{p}_1 \cdot \vec{r})(\vec{p}_2 \cdot \vec{r}) - r^2(\vec{p}_1 \cdot \vec{p}_2)}{r^5}$$

for one pair of dipole (elementary interaction):



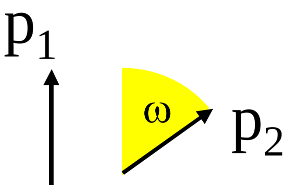
$$\left|U\right| \approx \frac{1}{4\pi\varepsilon_o} \frac{p^2}{r^3}$$

$|U|$ still $>$ $k_B T_c$!!!

Interactions

- **Dipolar interaction :** $U = -\vec{p}_2 \cdot \vec{E}(\vec{p}_1) = \frac{-1}{4\pi\varepsilon_o} \frac{3(\vec{p}_1 \cdot \vec{r})(\vec{p}_2 \cdot \vec{r}) - r^2(\vec{p}_1 \cdot \vec{p}_2)}{r^5}$

for an assembly of independent pairs:



$\omega(\theta_1, \varphi_1, \theta_2, \varphi_2)$ $\quad proba(\omega) \approx e^{-E(\omega)/k_B T}$

$$U \approx \frac{-1}{(4\pi\varepsilon_o)^2} \cdot \frac{p^4}{3k_B T r^6}$$

Van der Waals

depends on T

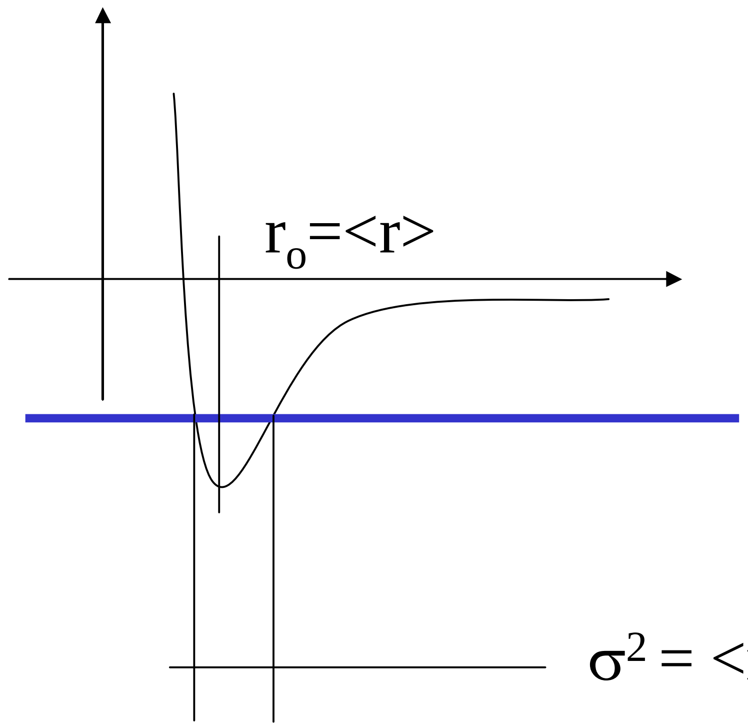
If $\frac{p^2}{<r>^3} > (4\pi\varepsilon_o) k_B T$ dipolar interaction becomes larger than thermal motion => **condensation** !!!

(noble gases condensation, ferroelectric waves in some dielectric materials…)

Interactions

- **Dipolar interaction :**

Lennard-Jones $$E_{pot} = \frac{A}{r^{12}} - \frac{B}{r^{6}}$$



Low Temp.

$$\sigma^2 = \langle r^2 \rangle - \langle r \rangle^2$$

Interactions

- **Magnetic interaction :**

Bohr magneton μ_B (9.3 10^{-24} Am^2) $\left(\frac{e\hbar}{2mc}\right)$

Magnetic moment (**electronic**) $\mu = -g\,\mu_B\,J = -g\,\mu_B\,(L+S)$

(Orbital and Spin momentum)

Pair interaction: U = -μ_2 B(μ_1) $\vec{B} = \frac{\mu_0}{4\pi}\,\frac{3\,(\vec{\mu}\cdot\vec{r})\,\vec{r}\;-\;r^2\,\vec{\mu}}{r^5}$

$|U| \approx \frac{\mu_o}{4\pi}\,\frac{\mu^2}{r^3}$

L=0

spin 1/2

g ~ 2

$\mu_o/4\pi = 10^{-7}$

U ~ 2μeV <<< k_BT

Only at very low temperature !!!

Interactions

- **Magnetic interaction :**

Nuclear magneton (5.05 10^{-27} Am^2) much lower than Bohr magneton

➔ Magnetic interaction would lead to phase transition at even lower temperatures !!!

- **Magnetic transition origin ?**

Electron exchange interaction

Quantum mechanics

$$H_o(\vec{r})\,\psi_\nu(\vec{r}) = \varepsilon_\nu\,\psi_\nu(\vec{r})$$

Two electrons wave function

$$\psi(\vec{r}_1,\vec{r}_2) = \varphi(\vec{r}_1,\vec{r}_2)\cdot\chi(\sigma_1,\sigma_2)$$

fermions ↓ *space* *spin*

Anti-symmetric → ***Anti-symmetric*** ***Symmetric***

→ ***Symmetric*** ***Anti-symmetric***

$$\psi(\vec{r}_1,\vec{r}_2) = -\psi(\vec{r}_2,\vec{r}_1)$$

Interactions

- **Magnetic transition origin :** **Electron exchange interaction**

Triplet state: $\chi(\sigma_1, \sigma_2)$ symmetric

$$\chi(\sigma_1, \sigma_2) = \left| \begin{array}{c} \uparrow\uparrow \\ \downarrow\downarrow \\ \uparrow\downarrow + \downarrow\uparrow \end{array} \right.$$

S=1

$$\varphi(\vec{r}_1, \vec{r}_2) = -\varphi(\vec{r}_2, \vec{r}_1)$$

$$\vec{r}_1 = \vec{r}_2 \quad \Rightarrow \quad \varphi(\vec{r}, \vec{r}) = -\varphi(\vec{r}, \vec{r}) = 0 \quad \Rightarrow \quad |\psi(\vec{r}, \vec{r})|^2 = 0$$

Pauli principle: *"two electrons with the same spin cannot be at the same place"*

Interactions

- **Magnetic transition origin :** **Electron exchange interaction**

Singlet state: $\chi\left(\sigma_1,\sigma_2\right)$ antisymmetric

$$\chi\left(\sigma_1,\sigma_2\right) = \uparrow\downarrow - \downarrow\uparrow$$

S=0

$$\varphi\left(\vec{r}_1,\vec{r}_2\right)=\varphi\left(\vec{r}_2,\vec{r}_1\right)$$

$$\vec{r}_1=\vec{r}_2 \quad\Rightarrow\quad \varphi\left(\vec{r},\vec{r}\right)=\varphi\left(\vec{r},\vec{r}\right)\neq 0 \quad\Rightarrow\quad \left|\psi\left(\vec{r},\vec{r}\right)\right|^2\neq 0$$

Pauli principle: *"two electrons with different spin can be at the same place"*

Interactions

- **Magnetic transition origin :** **Electron exchange interaction**

$$\psi_{\sigma_1\sigma_2}(\vec{r}_1,\vec{r}_2)=\frac{1}{\sqrt{2}}\left\{\psi_{1\sigma_1}(\vec{r}_1)\cdot\psi_{2\sigma_2}(\vec{r}_2)-\psi_{1\sigma_1}(\vec{r}_2)\cdot\psi_{2\sigma_2}(\vec{r}_1)\right\}$$

Single particle wave function

$$H_o(\vec{r})\,\psi_\nu(\vec{r})=\varepsilon_\nu\,\psi_\nu(\vec{r})$$ *Without interaction*

$$H=H_o(1)+H_o(2)+\frac{e^2}{4\pi\varepsilon_o|\vec{r}_1-\vec{r}_2|}$$ *With interaction*

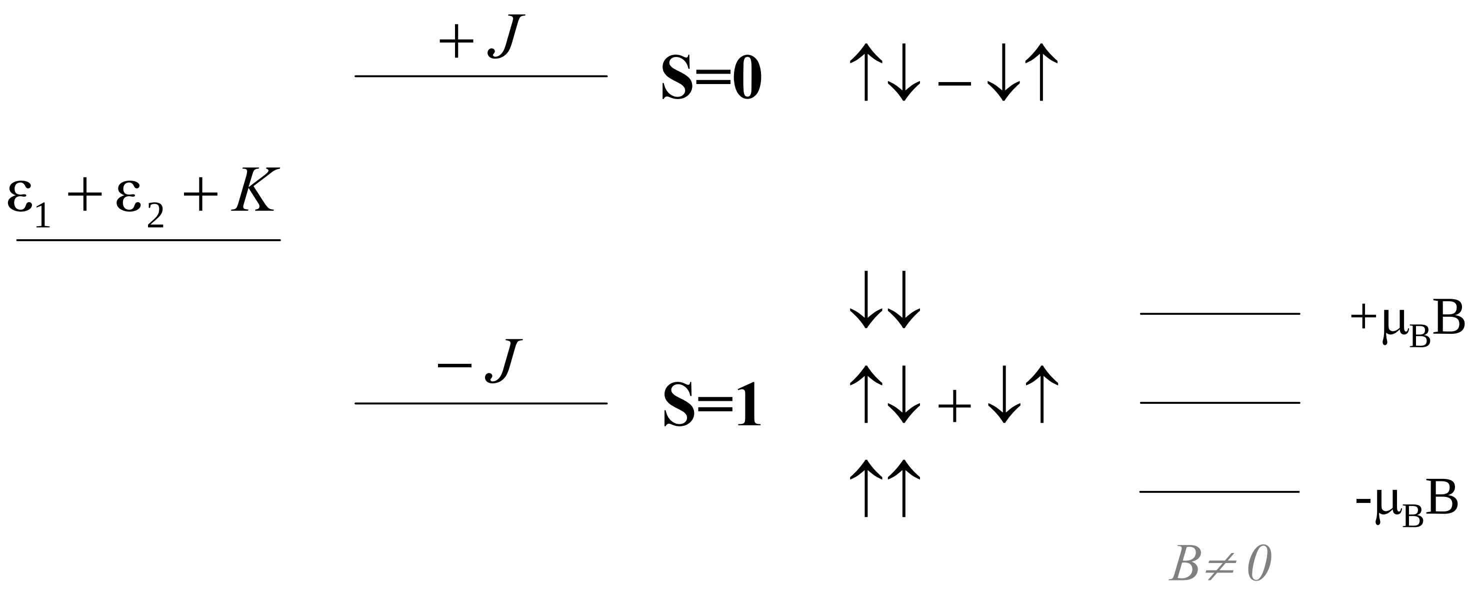
Solve $H\psi = E\psi$ … $$U=\varepsilon_1+\varepsilon_2+K\pm J$$

$$K=\iint|\psi_1(\vec{r}_1)|^2\frac{e^2}{4\pi\varepsilon_o|\vec{r}_1-\vec{r}_2|}|\psi_2(\vec{r}_2)|^2\,d^3r_1d^3r_2$$ *Coulomb integral*

$$J=\iint\psi_1^*(\vec{r}_1)\psi_2(\vec{r}_1)\frac{e^2}{4\pi\varepsilon_o|\vec{r}_1-\vec{r}_2|}\psi_1(\vec{r}_2)\psi_2^*(\vec{r}_2)\,d^3r_1d^3r_2$$ *Exchange integral*

Interactions

- **Magnetic transition origin :** **Electron exchange interaction**



Interactions

- **Magnetic transition origin :**

"Many sites interaction" $\mathrm{H} = \mathrm{H}_o + \mathrm{H}_{\mathrm{int}}^{\mathrm{eff}}$

$$\mathrm{H}_{\mathrm{int}}^{\mathrm{eff}} = -J \sum_{\nu\nu'} \sigma_\nu \sigma_{\nu'}$$

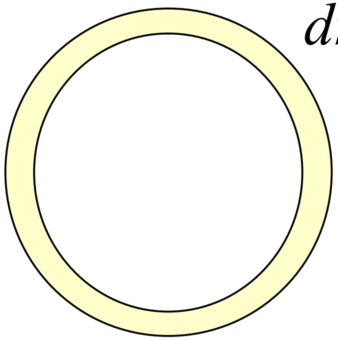
J can be of the order of $k_B T$: possible phase transitions with technological applications !!!

Interactions

- **Interaction range :**

Interaction strength scales like $\frac{1}{r^n}$

Homogeneous "pair distribution" : n(r)



$$dn = 4\pi\, r^2\, n(r)\, dr$$

$$\mathrm{U}_{\mathrm{tot}} \sim \int \frac{dr}{r^{n-2}}$$

Convergence if n > 3 !!!

Interactions

- **Interaction range :**

Dipolar interaction n=3 : asymptotic convergence

van der Waals n=6 : good convergence: short range interaction

Exchange interaction: short range

Atomic orbitals' radial functions ~ $r^n e^{-\varsigma r}$ *(Slater function)*