I 1/20

V.1.5 Example (mixed system)

Ideal gas of N identical atoms in box of volume V.
each atom has spin $\frac{1}{2}$ and magnetic moment μ.
external magnetic field $\vec{H}$

State of the system: $(\vec{x}^N, s_1, \ldots, s_N)$ $\quad s_i = \pm 1$

Energy : $E(\vec{x}, s_1, \ldots, s_N) = \frac{1}{2m}\sum_{i=1}^{N} \vec{p}_i^{\,2} - \frac{1}{2}\mu H \sum_{i=1}^{N} s_i$

partition function:

$$Z(T) = \frac{1}{c_N}\int d\vec{x}^N \sum_{\{(s_1,\ldots,s_N)\}} e^{-\frac{\beta}{2m}\sum_{i=1}^{N}\vec{p}_i^{\,2} + \frac{\beta\mu H}{2}\sum_{i=1}^{N} s_i}$$

$$= \frac{V^N}{N!\,h^{3N}} \int d\vec{p}_1 \ldots \int d\vec{p}_N \sum_{s_1\in\{-1,1\}} \ldots \sum_{s_N\in\{-1,1\}} e^{-\frac{\beta}{2m}\sum_{i=1}^{N}\vec{p}_i^{\,2} + \frac{\beta\mu H}{2}\sum_{i=1}^{N} s_i}$$

$$= \frac{V^N}{N!\,h^{3N}} \left(\int d\vec{p}\, e^{-\frac{\beta}{2m}\vec{p}^{\,2}}\right)^N \left(e^{-\frac{\beta\mu H}{2}} + e^{\frac{\beta\mu H}{2}}\right)^N$$

$$= \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} \left(2\cosh\left(\frac{\beta\mu H}{2}\right)\right)^N$$

I 1/15

$$\ln Z(T) = N\left\{1 + \ln\left[\frac{2V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\right] + \ln\cosh\frac{\beta\mu H}{2}\right\}$$

internal energy:

$$U = -\frac{\partial \ln Z}{\partial\beta} = +\frac{3}{2}N\frac{1}{\beta} - N\frac{\sinh\frac{\beta\mu H}{2}}{\cosh\frac{\beta\mu H}{2}}\frac{\mu H}{2}$$

$$= \frac{3}{2}N k_B T - \frac{N\mu H}{2}\tanh\frac{\beta\mu H}{2}$$

Heat capacity:

$$C_{V,N,H} = \left(\frac{\partial U}{\partial T}\right)_{V,N,H} = \frac{3}{2} N k_B + \frac{1}{k_B T^2}\left(\frac{\partial}{\partial \beta} \tanh \frac{\beta \mu H}{2}\right)_{V,N,B} \frac{N\mu H}{2}$$

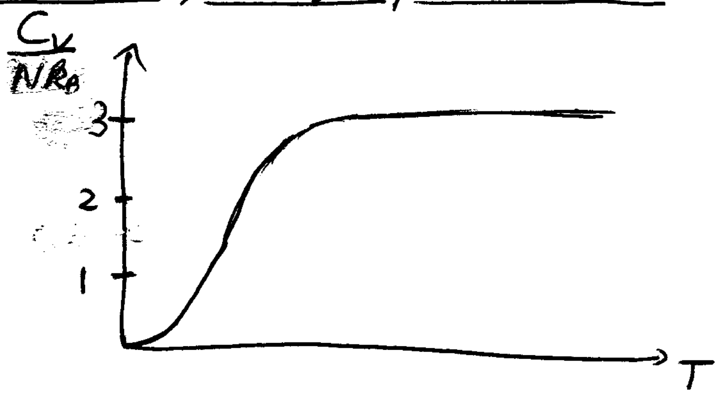
$$= \frac{3}{2} N k_B + \frac{N}{k_B T^2}\left(\frac{\mu H}{2}\right)^2 \frac{1}{\cosh^2 \frac{\beta\mu H}{2}}$$

magnetization:

$$M = -\left(\frac{\partial F}{\partial H}\right)_{T,N,V} = k_B T \left(\frac{\partial \ln Z}{\partial H}\right)_{T,V,N}$$

$$= k_B T N \frac{\beta\mu}{2} \frac{\sinh \frac{\beta\mu H}{2}}{\cosh \frac{\beta \mu H}{2}} = \frac{1}{2} N \mu \tanh \frac{\beta \mu H}{2}$$

V.2 Heat capacity of a solid



measured heat capacities

Where does heat capacity come from?

→ where does internal energy of a solid come from?

→ oscillations of the atoms

Model I: every atom oscillates independently and harmonically around equilibrium position $\vec{r}_{0i}$

$$H(\vec{x}^N) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \frac{1}{2} m \omega^2 \sum_{i=1}^{N} (\vec{r}_i - \vec{r}_{0i})^2$$

$$Z(T) = \frac{1}{C_N}\int d\vec{x}^N e^{-\frac{\beta}{2m}\sum_{i=1}^{N}\vec{p}_i^2 - \frac{\beta m\omega^2}{2}\sum_{i=1}^{N}(\vec{r}_i - \vec{r}_{0,i})^2}$$

$$= \frac{1}{h^{3N}}\int d\vec{p}_1 e^{-\frac{\beta}{2m}\vec{p}_1^2}\cdots\int d\vec{p}_N e^{-\frac{\beta}{2m}\vec{p}_N^2}\int d\vec{r}_1 e^{-\frac{\beta m\omega^2}{2}(\vec{r}_1-\vec{r}_{1,0})^2}\cdots\int d\vec{r}_N e^{-\frac{\beta m\omega^2}{2}(\vec{r}_N-\vec{r}_{0,N})^2}$$

$$= \frac{1}{h^{3N}}\left(\int d\vec{p}\, e^{-\frac{\beta}{2m}\vec{p}^2}\right)^N\left(\int d\vec{r}\, e^{-\frac{\beta m\omega^2}{2}\vec{r}^2}\right)^N$$

$$= \frac{1}{h^{3N}}(2\pi m k_B T)^{3/2 N}\left(\frac{2\pi k_B T}{m\omega^2}\right)^{3/2 N} = \left(\frac{2\pi k_B T}{h\omega}\right)^{3N} = \left(\frac{k_B T}{\hbar\omega}\right)^{3N}$$

$$U = -\left(\frac{\partial \ln Z}{\partial\beta}\right)_{V,N} = -\left(\frac{\partial}{\partial\beta}\left[-3N\ln\beta\hbar\omega\right]\right) = \frac{3N}{\beta} = 3Nk_BT$$

$$C_{V,N} = \left(\frac{\partial U}{\partial T}\right)_{V,N} = 3Nk_B$$

- independent of T
- explains experimental data at high temperatures

Why is behavior at low temperatures different?

At low temperatures (= low energies) oscillations cannot take any energy because of the quantum nature of the oscillators.

→ vanishing C_T is manifestation of quantum mechanics in a <u>macroscopic</u> variable!

<u>Model II</u>: same as model I, but treat oscillators quantum mechanically

→ Einstein solid

$$C_N = \frac{3N(\hbar\omega)^2}{k_BT^2}\frac{e^{-\frac{\hbar\omega}{k_BT}}}{\left(1-e^{-\frac{\hbar\omega}{k_BT}}\right)^2}$$

$$C_N \xrightarrow[k_BT \gg \hbar\omega]{} \frac{3N(\hbar\omega)^2}{k_B T^2} \frac{1}{\left(\frac{\hbar\omega}{k_BT}\right)^2} = 3Nk_B \quad \checkmark$$

$$C_N \xrightarrow[k_BT \ll \hbar\omega]{} \sim \frac{1}{T^2} e^{-\frac{\hbar\omega}{k_BT}} \longrightarrow 0$$

experimentally for small T: $\quad C_N \sim \frac{1}{T^3}$

→ need better theory → coupled oscillators $\qquad$ 11/20

<u>Model III</u>: Debye solid

consider solid as an <u>elastic medium</u>

of size $L_x L_y L_z$

→ possible oscillation modes are standing waves

wavelengths $\frac{2L_x}{l_x}, \frac{2L_y}{l_y}, \frac{2L_z}{l_z}$ with integers l_x, l_y, l_z

frequency of the mode of type i (2 transverse, 1 longitudinal)

$$\omega^2_{(l_x, l_y, l_z, i)} = c_i^2 \left[\left(\frac{\pi l_x}{L_x}\right)^2 + \left(\frac{\pi l_y}{L_y}\right)^2 + \left(\frac{\pi l_z}{L_z}\right)^2 \right]$$

energy of the system

$$H = \sum_{(l_x, l_y, l_z, i)} \hbar\omega_{(l_x, l_y, l_z, i)} \left(n_{(l_x, l_y, l_z)} + \tfrac{1}{2} \right)$$

number of quanta in mode (l_x, l_y, l_z)

partition function:

$$Z(T) = \sum_{\{n_{(l_x, l_y, l_z, i)}\}} e^{-\beta \sum_{(l_x, l_y, l_z, i)} \hbar\omega_{(l_x, l_y, l_z, i)} \left(n_{(l_x, l_y, l_z)} + \frac{1}{2}\right)}$$

$$= \prod_{l_x, l_y, l_z, i} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega_{(l_x, l_y, l_z, i)}\left(n + \frac{1}{2}\right)}$$