PHYS 3014: Statistical Mechanics

Lecture Notes
Part 9

Canonical Ensemble: Two level systems, negative temperature

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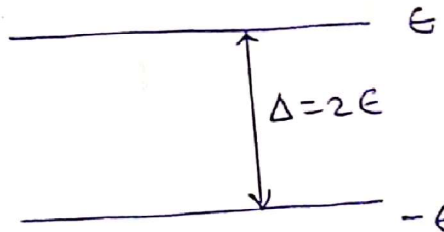
Two level System ; Specific Heat, Negative Temperature

Consider a system of N dipoles with $J=\frac{1}{2}$. Each dipole has to be in one orientation either up or down. In external magnetic field the energies of dipoles are either $-\mu_B H$ or $\mu_B H$ i.e $-\epsilon$ or ϵ.



The partition function of the system is

$$Z(T,V,N) = \left[e^{\beta\epsilon} + e^{-\beta\epsilon}\right]^N$$

$$= \left[2\cosh(\beta\epsilon)\right]^N$$

Helmholtz free energy

$$F(T,V,N) = -KT\ln\{Z(T,V,N)\} = -NKT\ln\left[e^{\beta\epsilon}+e^{-\beta\epsilon}\right]$$

$$= -NKT\ln\left[2\cosh(\beta\epsilon)\right]$$

Entropy of the system $S(T,V,N) = -\left(\frac{\partial F}{\partial T}\right)_{N,V}$

or $$S(T,V,N) = NK \ln\left[e^{\beta\epsilon} + e^{-\beta\epsilon}\right] + \frac{NKT \; \epsilon\left[e^{\beta\epsilon} - e^{-\beta\epsilon}\right]}{\left(e^{\beta\epsilon} + e^{-\beta\epsilon}\right)} \cdot \left(-\frac{1}{KT^2}\right)$$

$$= NK \ln\left[e^{\beta\epsilon} + e^{-\beta\epsilon}\right] - NK\beta\epsilon \tanh(\beta\epsilon)$$

$$= NK\left[\ln\{2\cosh(\beta\epsilon)\} - \beta\epsilon \tanh(\beta\epsilon)\right]$$

Energy of the system

$$U = F + TS$$

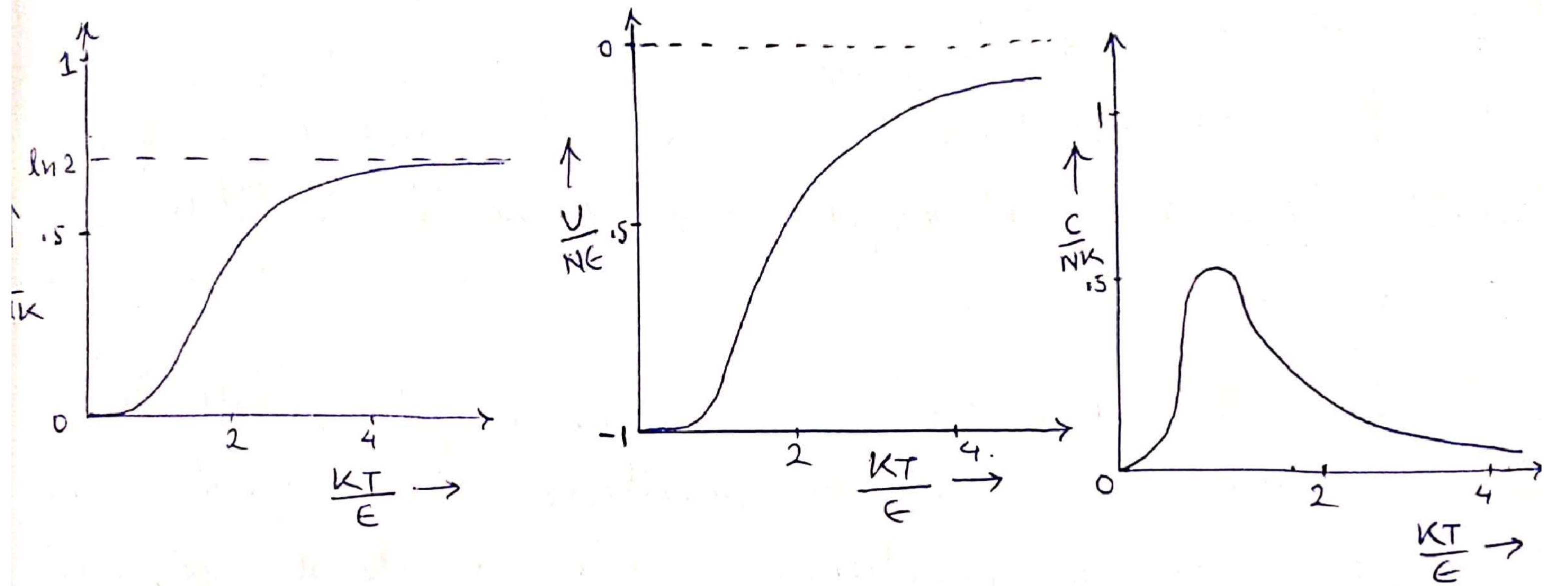
$$= -N\epsilon \tanh(\beta\epsilon) = -\epsilon \times \text{Effective no. of dipoles}$$

Specific heat

$$C = \left(\frac{\partial U}{\partial T}\right)_H = NK \sec^2(\beta\epsilon) \cdot (\epsilon\beta)^2$$

The temperature dependence of S, U and C are shown in figures.

When $KT << \epsilon$ i.e $\beta\epsilon >> 1$ then $S \to 0$ i.e entropy of the system is vanishingly small.



S rises rapidly when $KT \simeq \epsilon$ and when $KT >> \epsilon$

i.e $\beta\epsilon << 1$ then $S \to NK \ln 2$.

At high temperatures, dipoles are randomly oriented and each dipole has two possible modes to orient. So the total microstates will be $2 \times 2 \times 2 \cdots$ N times $= 2^N$

$\therefore \quad S = K \ln 2^N = NK \ln 2$.

when $T \to 0$, $U \to -N\epsilon$ i.e all dipoles are present in ground state representing a state of magnetic saturation which is a state of perfect order in the system.

At high temperatures, $U \to 0$. It implies a purely random orientation of dipoles and hence a complete loss of magnetic order.

At low temperature, C is vanishingly small. It also vanishes at high temperatures. It is quite obvious that at high temperatures, energy of system approaches a constant value.

Now

$$C = NK \operatorname{sech}^2(\beta\epsilon) \cdot (\beta\epsilon)^2 \qquad \because \Delta = 2\epsilon$$

$$= \frac{NK(2\epsilon\beta)^2}{(2\cosh\beta\epsilon)^2} = NK\left(\frac{\Delta}{KT}\right)^2 \cdot \frac{1}{(e^{\beta\epsilon}+e^{-\beta\epsilon})^2}$$

$$= NK\left(\frac{\Delta}{KT}\right)^2 \cdot \frac{e^{2\beta\epsilon}}{(1+e^{2\beta\epsilon})^2} = NK\left(\frac{\Delta}{KT}\right)^2 \cdot \frac{e^{\frac{\Delta}{KT}}}{(1+e^{\frac{\Delta}{KT}})^2}$$

Δ is the energy difference between the two allowed energy states ϵ and $-\epsilon$ of the system.

The specific heat having the above form is called as Schottky specific heat. It has a characteristic anomalous peak and observed in all systems with an excitation gap Δ.

For studying the variation of temperature T and entropy S with the energy U of the system, we have

$$\frac{1}{T} = -\frac{K}{\epsilon} \tanh^{-1}\left(\frac{U}{N\epsilon}\right) \qquad \because \tanh^{-1}(x) = \frac{1}{2}\ln\left(\frac{1+x}{1-x}\right)$$

when $-1 < x < 1$

$$= -\frac{K}{2\epsilon} \ln\left[\frac{1+\frac{U}{N\epsilon}}{1-U/N\epsilon}\right]$$

$$= \frac{K}{2\epsilon} \ln\left(\frac{N\epsilon - U}{N\epsilon + U}\right)$$

and

$$\frac{S}{NK} = \ln\left\{2\cosh\left(\frac{\epsilon}{KT}\right)\right\} - \frac{\epsilon}{KT}\tanh\left(\frac{\epsilon}{KT}\right)$$

$$= \ln\left\{2\cosh\left(\frac{\epsilon}{KT}\right)\right\} - \tanh^{-1}\left(-\frac{U}{N\epsilon}\right)\cdot\left(\frac{-U}{N\epsilon}\right)$$

$$\frac{S}{NK} = \ln\left\{2\cosh\left(\frac{\epsilon}{KT}\right)\right\} - \left(\frac{U}{N\epsilon}\right)\tan^{-1}\left(\frac{U}{N\epsilon}\right)$$

$$\cosh x = \frac{1}{\sqrt{1-\tanh^2 x}}$$

$$= \ln\left\{\frac{2}{\sqrt{1-\tanh^2\left(\frac{\epsilon}{KT}\right)}}\right\} - \left(\frac{U}{N\epsilon}\right)\tan^{-1}\left(\frac{U}{N\epsilon}\right)$$

$$= \ln\left\{\frac{2N\epsilon}{\sqrt{(N\epsilon)^2 - U^2}}\right\} - \frac{U}{2N\epsilon}\ln\left(\frac{N\epsilon+U}{N\epsilon-U}\right)$$

$$= \ln(2N\epsilon) - \frac{1}{2}\ln(N\epsilon-U) - \frac{1}{2}\ln(N\epsilon+U) - \frac{U}{2N\epsilon}\ln(N\epsilon+U)$$
$$+ \frac{U}{2N\epsilon}\ln(N\epsilon-U)$$

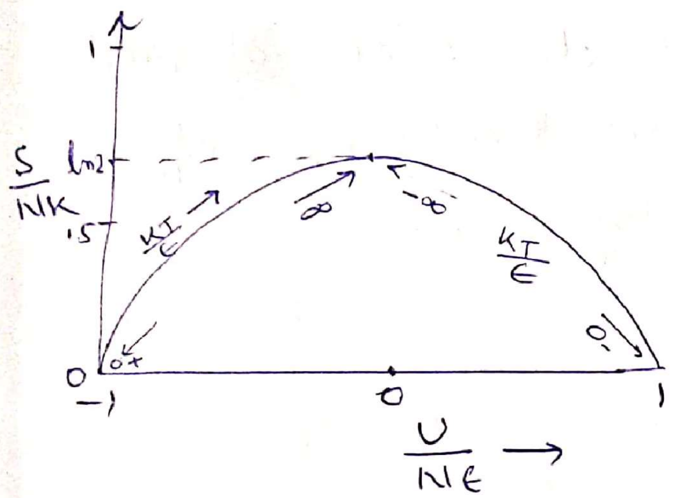
$$= -\left(\frac{N\epsilon+U}{2N\epsilon} + \frac{N\epsilon-U}{2N\epsilon}\right)\ln\left(\frac{1}{2N\epsilon}\right) + \left[\frac{U-N\epsilon}{2N\epsilon}\right]\ln(N\epsilon-U)$$
$$- \left(\frac{U+N\epsilon}{2N\epsilon}\right)\ln(N\epsilon+U)$$

$$\therefore \frac{S}{NK} = -\left(\frac{N\epsilon+U}{2N\epsilon}\right)\ln\left(\frac{N\epsilon+U}{2N\epsilon}\right) - \left(\frac{N\epsilon-U}{2N\epsilon}\right)\ln\left(\frac{N\epsilon-U}{2N\epsilon}\right)$$

when $U = -N\epsilon$, then $S = 0$

and $T = 0$

When U increases and becomes 0 then S obtains its maximum value ln 2 whereas temperature becomes ∞.



for range of $\frac{U}{NE}$ i.e from -1 to 0 entropy is monotonically increasing function of energy. Temperature varies from +0 to $+\infty$.

When U becomes 0_+ then slope of $\frac{\partial S}{\partial U}$ changes and becomes -ive and temperature becomes $-\infty$. With further increase in U, entropy decreases monotonically and temperature remains negative and its magnitude decreases steadily. When $\frac{U}{NE}$ becomes +1 then entropy once again becomes 0 and temperature becomes -0.

So we are getting a situation when energy $U > 0$ i.e in the upper level particles are more in comparison to lower level where temperature of the system becomes negative. The system is then in the state of negative temperature. The onset of negative temperature is possible when there exists an upper limit on the energy of the system.

A simple two level system with energies 0 and ϵ. whose degeneracies are 1 and 2 respectively.

The single particle partition function

$$Z(T,V,1) = \sum_r g_r e^{-\beta \epsilon_r}$$

$$= 1 + 2e^{-\beta\epsilon}$$

For N particle system

$$Z(T,V,N) = [Z(T,V,1)]^N$$ particles are distinguishable.

$$= [1+2e^{-\beta\epsilon}]^N$$

$\therefore$ Helmholtz free energy $F(T,V,N) = -KT \ln\{Z(T,V,N)\}$

or, $F(T,V,N) = -NKT \ln(1+2e^{-\beta\epsilon})$

Entropy $S(T,V,N) = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = -\left(\frac{\partial F}{\partial \beta}\right)_{V,N}\left(\frac{\partial \beta}{\partial T}\right)$

$$= NK \ln(1+2e^{-\beta\epsilon}) + NKT \cdot \frac{1 \cdot 2e^{-\beta\epsilon}(\epsilon)}{1+2e^{-\beta\epsilon}} \cdot \left(-\frac{1}{KT^2}\right)$$

$$= NK\left[\ln(1+2e^{-\beta\epsilon}) + \frac{2\beta\epsilon}{2+e^{\beta\epsilon}}\right]$$

Energy of the system $U = F + TS$

or, $$U = -NKT\ln(1+2e^{-\beta\epsilon}) + NKT\ln(1+2e^{-\beta\epsilon}) + \frac{NKT \cdot 2\beta\epsilon}{2+e^{\beta\epsilon}}$$

or, $$U = \frac{2N\epsilon}{e^{\beta\epsilon}+2}$$

References:

- Statistical Mechanics by R. K. Pathria
- Statistical Mechanics by B. K. Agarwal and M. Eisner
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- Elementary Statistical Physics by C. Kittel
- Fundamentals of Statistical and Thermal Physics by F. Reif
- Statistical and Thermal Physics by R. S. Gambhir and S. Lokanathan

Thank You

For any questions/doubts/suggestions and submission of assignments

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