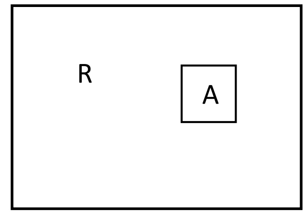
Canonical Ensemble (Chap. 5)

Previous considerations kept E, N, V fixed and counted number of configurations.

Now allow E of a system to vary by passing energy to neighbors

Take system A to be specified in quantum state $|\psi_i >$ and embedded in reservoir R

Total system has internal energy $U_T = U_A + U_R$ which IS a constant



$$U_R = U_T - U_A$$

Number of accessible states for combined system is

$W(U_A) = W_A(U_A)W_R(U_R) = W_A(U_A)W_R(U_T - U_A)$..........................(1)

$W_A(U_A)$ is number of states of A that have energy U_A. $W_R(U_T - U_A)$ is no. of states of R that have energy $U_T - U_A$.

By construction $U_A = E_i$ the energy eigenvalue for the state $|\psi_i >$. It is a single state

So $W_A(E_i) = 1$ for A. For total states, from (1) above $W(E_i) = 1 \times W_R(U_T - E_i)$ ....(2)

Now find reservoir temperature using $\frac{1}{k_BT} = \left(\frac{\partial lnW_R}{\partial U_R}\right)_V$ which implies $W_R = \gamma e^{U_R/k_BT}$

Eq'n (2) is now used to write $W(E_i) = \gamma e^{(U_T - E_i)/k_BT}$

Fundamental postulate

All accessible states are equally likely

$$N = \sum_i W(E_i) = \gamma\left(e^{\frac{U_T}{k_BT}}\right)\sum_i e^{-\frac{E_i}{k_BT}}$$

Probability that particle in state $|\psi_i >$

$$p_i = \frac{W(E_i)}{\sum_i W(E_i)} = \frac{e^{-\frac{E_i}{k_BT}}}{Z}$$

DEFINES PARTITION FUNCTION

$$z = \sum_i e^{-\frac{E_i}{k_BT}}$$

If states have degeneracy g_i then

$$z = \sum_i g_i e^{-\frac{E_i}{k_BT}}$$

Gibbs Ensemble

Consider system A in thermal contact with M-1 replica systems (called Gibbs ensemble)

Calculate no. of ways can have n_1 replicas in ψ_1, n_2 in ψ_2, n_3 in ψ_3 etc.

No of ways $W = \frac{M!}{n_1!n_2!n_3!.........}$

For the Gibbs ensemble $S_M = k_B lnW = k_B[MlnM - \sum_i n_i ln(n_i)]$

$$S_M = -k_B M \sum_i \frac{n_i}{M} \ln\left(\frac{n_i}{M}\right)$$

Entropy for system $S = \frac{S_M}{M} = -k_B \sum_i p_i \ln p_i$

Note if all $p_i = \frac{1}{W}$ $S = +k_B lnW$ as expected

Bridge to thermodynamics

For canonical ensemble have established that probability of occurrence for state ψ_1 is $p_i = \frac{e^{-E_i/k_BT}}{Z}$

Or $lnp_i = -\frac{E_i}{k_BT} - lnZ$ thus $S = -k_B \sum_i p_i \ln p_i = k_B \sum_i p_i \left[\left(\frac{E_i}{k_BT}\right) + lnZ\right]$

Find $S = \frac{U}{T} + k_B lnZ$ $U - TS = -k_B lnZ$

Now have expression for Helmholtz Free Energy

$$F = -k_B lnZ$$

THERMODYNAMIC QUANTITIES

$$dF = -PdV - SdT$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = k_B\left[\frac{\partial}{\partial V}(TlnZ)\right]_T$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = k_B\left[\frac{\partial}{\partial T}(TlnZ)\right]_V$$

Now find useful measurable parameters in terms of second derivatives:

Isothermal compressibility

$$K^{-1} = -V\left(\frac{\partial P}{\partial V}\right)_T = V\left(\frac{\partial^2 F}{\partial V^2}\right)_T$$

Heat capacity

$$C = T\left(\frac{\partial S}{\partial T}\right)_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_T$$

Internal energy

$$U = TS + F$$

$$U = k_B T^2\left(\frac{\partial}{\partial T}(lnZ)\right)_V$$

If know states and their energies and degeneracy can calculate Z and thus the measurable parameters

Example: **Schottky Energy Levels**

(Occurs often in modern experiments); e.g. nuclear spin heat capacities at low temperatures

Two non-degenerate energy levels at $+\varepsilon$, $-\varepsilon$

$$Z = e^{-\frac{\varepsilon}{k_B T}} + e^{\frac{\varepsilon}{k_B T}} = 2cosh\left(\frac{\varepsilon}{k_B T}\right)$$

Helmholtz Free Energy

$$F = -k_B T lnZ = -k_B T ln2 - k_B T ln\left[cosh\left(\frac{\varepsilon}{k_B T}\right)\right]$$

Entropy

$$S = -\frac{\partial F}{\partial T} = k_B ln2 + k_B ln\left[cosh\left(\frac{\varepsilon}{k_B T}\right)\right] - \frac{\varepsilon}{T} tanh\left(\frac{\varepsilon}{k_B T}\right)$$

$$S \dashrightarrow k_B ln2 \quad as\, T \dashrightarrow \infty$$

$$S \dashrightarrow 0 \quad as\, T \dashrightarrow 0$$

Internal Energy

$U = F + TS = -\varepsilon\, tanh\left(\frac{\varepsilon}{k_B T}\right)$ Similar to magnetization (as expected)

Heat capacity

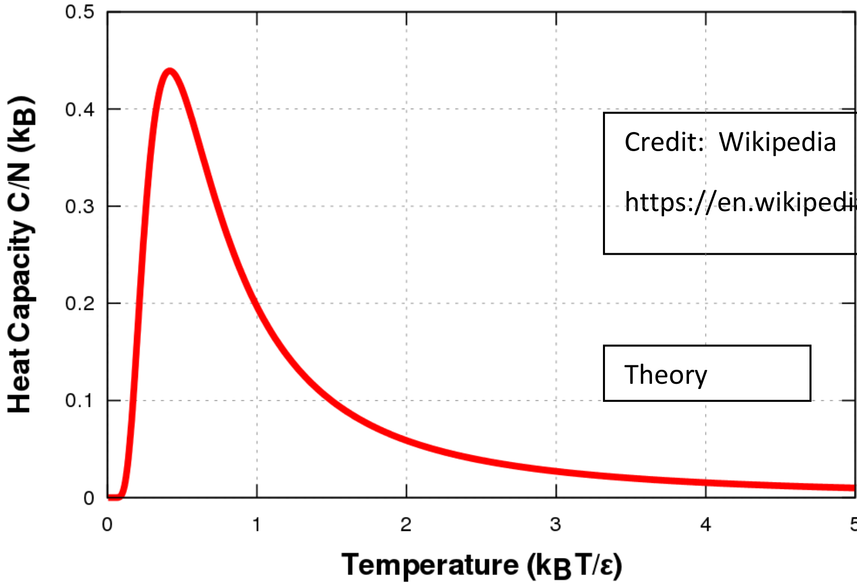
$$C = T\left(\frac{\partial S}{\partial T}\right)_V = T\left\{\frac{\sinh\left(\frac{\varepsilon}{k_B T}\right)}{\cosh\left(\frac{\varepsilon}{k_B T}\right)}\left(-\frac{\varepsilon}{k_B T^2}\right) + \frac{\varepsilon}{T^2}\tanh\left(\frac{\varepsilon}{k_B T}\right) - \frac{\varepsilon}{T}\frac{1}{cosh^2(\frac{\varepsilon}{k_B T})}\left(-\frac{\varepsilon}{k_B T^2}\right)\right\}$$

Finally,

$$\boxed{C = \frac{\varepsilon}{k_B T^2}\frac{1}{cosh^2(\frac{\varepsilon}{k_B T})}}$$

At low T, C is exponential $C \propto e^{-\frac{2\varepsilon}{k_B T}}$, high T $C \propto T^{-2}$

Has a broad peak at $T \sim 0.7\varepsilon$



Credit: Wikipedia

https://en.wikipedia.org/wiki/Schottky_anomaly

Theory

Usually not so clear. Typically large phonon contribution that need to be subtracted to see Schottky capacities if they are resent

Example

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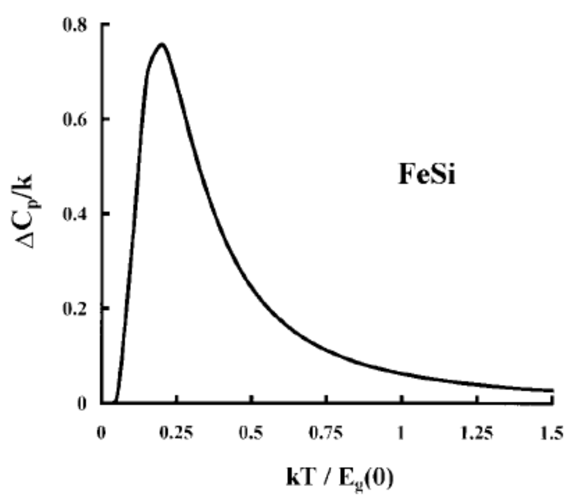

Figure 1. The temperature dependence of the specific heat anomaly in FeSi, as determined in [25]. The quantity $E_g(0)$ is the energy gap.

[25] JACCARINO, V., WERTHEIM, G. K., WERNICK, J. H., and WALKER, L. R., 1967, *Phys. Rev.*, **160**, 476.

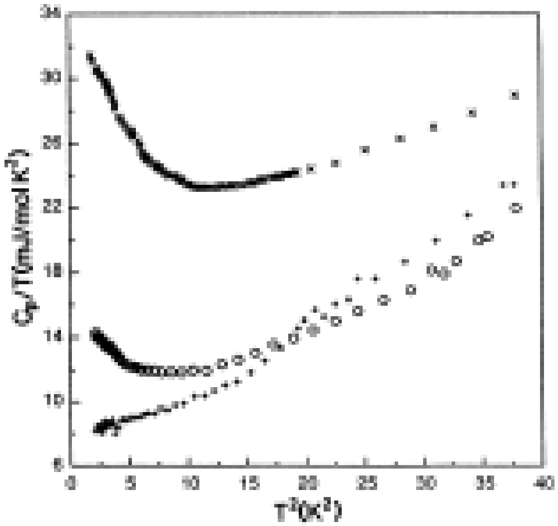

FIG. 1. C_p/T vs T^2. The symbols are as follows: + for sample A, ○ for sample B, and × for the data of Junod *et al.* (Ref. 4).

Schottky anomaly in the heat capacity of the high-T_c superconductor $YBa_2Cu_3O_7$

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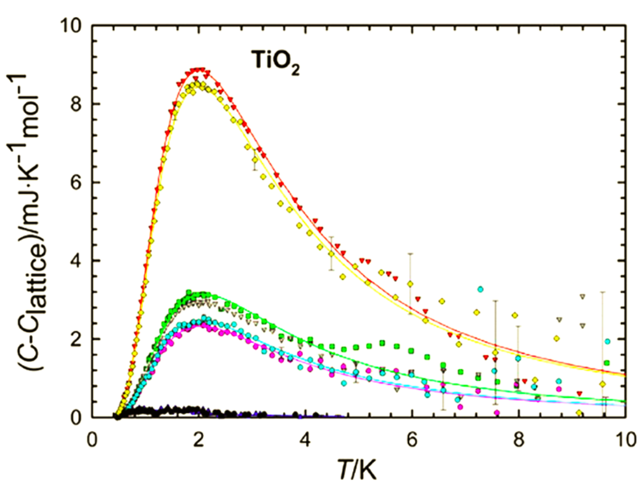

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HOH at defect sites and tunneling of OH group leads to splitting of ground state

Single Particle on a 1D Box.

Wave function determined by boundary conditions.

$$\varphi_n(x) = A\, sin\frac{n\pi x}{L}$$

n=1, 2, 3, 4

Energy eigenvalues: $\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\varphi_n(x) = E_n\varphi_n(x)$

$E_n = \left(\frac{\hbar^2\pi^2}{2mL^2}\right)n^2 = \alpha n^2$ where $\alpha = \frac{\hbar^2\pi^2}{2mL^2}$

Partition function

$$Z = \sum_{n=1}^{\infty} e^{-\left(\frac{\alpha n^2}{k_B T}\right)} = \sum_{n=1}^{\infty} e^{-\gamma n^2}$$

$$\gamma = \frac{\alpha}{k_B T}$$

N.B. α is very small ~ 1K (10^{-23} J) for proton in 1 micrometer.

Homework: Calculate α for ^{4}He atom in 10 Å.

Need to sum to large n

Replace sum by integral

$$Z = \int_0^{\infty} e^{-\gamma n^2} = \left(\frac{\pi}{4\gamma}\right)^{1/2}$$

Result for 1D translational motion

$Z_{1D}^{trans} = \frac{L}{\lambda_D}$ $\lambda_D = \left(\frac{2\pi\hbar^2}{mk_B T}\right)^{\frac{1}{2}}$ ~ 5 Å at 1 K. is the de Broglie wavelength

Thermodynamic properties for 1D

Free Energy $F = -k_B T ln Z = -k_B T ln \frac{L}{\lambda_D}$ $\quad ln\lambda_D = constant - \frac{1}{2} lnT$

Entropy $S = -\left(\frac{\partial F}{\partial T}\right)_V = k_B ln\frac{L}{\lambda_D} + k_B T \frac{1}{\lambda_D}\frac{\partial \lambda_D}{\partial T}$

Seek measurable quantitities

Heat capacity

$$C_V = T\frac{\partial S}{\partial T} = k_B T^2 \frac{\partial}{\partial T} ln\frac{\lambda_D}{T}$$

Find $C_V = \frac{k_B}{2}$ for 1D translational motion (free particle)

<u>Three dimensional box</u>

Wave function obeys boundary conditions in x, y and z directions

$$\psi(x,y,z) = A\, sin\frac{n_1 \pi x}{L}\; sin\frac{n_2 \pi y}{L}\; sin\frac{n_3 \pi z}{L}$$

n_1, n_2, n_3 independent integers that specify the wave function $\psi(n_1, n_2, n_3)$

Energy eigenvalues:

$$E(n_1, n_2, n_3) = \left(\frac{\hbar^2 \pi^2}{2mL^2}\right)[n_1^2 + n_2^2 + n_3^2]$$

Partition function

$Z_{trans}^{3D} = \sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\sum_{n_2=1}^{\infty} e^{-\gamma[n_1^2+n_2^2+n_3^2]}$

or $\quad Z = (\sum_{n_1=1}^{\infty} e^{-\gamma {n_1}^2})(\sum_{n_2=1}^{\infty} e^{-\gamma {n_2}^2})(\sum_{n_3=1}^{\infty} e^{-\gamma {n_3}^2})$

and thus simply $\quad Z_{trans}^{3D} = L^3 \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2} = V\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2}$

We have $\quad Z_{trans}^{3D} = (Z_{trans}^{1D})^3$

Free energy $F = -k_B T lnZ = -k_B T \left[lnV + \frac{3}{2} ln\left(\frac{mk_BT}{2\pi\hbar^2}\right)\right]$

Now find **pressure** from

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{k_B T}{V}$$

For N particles $PV = Nk_B T$

To find entropy

start with $F = -k_B T lnZ = -k_B T \left[lnV + \frac{3}{2} lnT + \frac{3}{2} ln\left(\frac{mk_B}{2\pi\hbar^2}\right)\right]$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = k_B \left[lnV + \frac{3}{2} lnT + \frac{3}{2} ln\left(\frac{mk_B}{2\pi\hbar^2}\right)\right] + k_B T \frac{3}{2T}$$

Heat capacity

$$C_V^{3D} = T\left(\frac{\partial S}{\partial T}\right)_V = \frac{3}{2} k_B$$

For particle in a box

Can relate gas product PV to average internal energy

Energy

$$E(n_1, n_{so2}, n_3) = \left(\frac{\hbar^2\pi^2}{2mL^2}\right)[n_1^2 + n_2^2 + n_3^2] = \left(\frac{\hbar^2\pi^2}{2m}\right)V^{-\frac{2}{3}}[\ldots\ldots]$$

So $\frac{\partial E}{\partial V} = -\frac{2}{3}\frac{E}{V}$

Work $dW = -PdV = \sum_i p_i dE_i = \sum_i p_i \frac{\partial E_i}{\partial V} dV = -\frac{2}{3}\frac{1}{V}(\sum_i p_i E_i)dV$

Find $\boldsymbol{PV = \frac{2}{3} U_{avg}}$

Equipartition

Since we cannot specify position q and momentum p precisely because of the uncertainty principle, we divide (q,p) phase space into a series of very small (but finite volume) cells (dq.dp).

Now write partition function $Z = \frac{1}{h}\int_0^\infty dq \int_0^\infty dp\, e^{-E(q,p)/k_B T}$

In many practical cases the energy can be expressed as a sum of quadratics

$$E(p,q) = aq^2 + bp^2$$

And following the same steps as above we have

$$Z = \frac{1}{h^{1/2}}\int_0^\infty dq e^{-\frac{aq^2}{k_B T}} \quad \frac{1}{h^{1/2}}\int_0^\infty dp e^{-\frac{ap^2}{k_B T}}$$

$$Z = \left(\frac{\pi k_B T}{ha}\right)^{\frac{1}{2}} \left(\frac{\pi k_B T}{hb}\right)^{\frac{1}{2}}$$

Calculate heat capacity as above to find each factor contributes $\frac{k_B}{2}$ to C_V

Example

LCR resonant circuit

For a parallel LC resonant circuit the voltage across the inductance – RF energy oscillates between inductance and capacitance $\omega^2 = 1/LC$

voltage across capacitance (neglecting small resistance losses)=voltage across inductance

$$v = -L\frac{dI}{dt} = \frac{Q}{C}$$

$$L\frac{d^2}{dt^2}Q + \frac{Q}{C} = 0$$

$$L\dot{Q}\ddot{Q} + C^{-1}Q\dot{Q} = 0$$

Whence $\frac{L}{2}(\dot{Q})^2 + \frac{1}{2}C^{-1}Q^2 = constant$

Thus $\frac{1}{2}L\langle I^2\rangle = \frac{k_B}{2}$ **Current noise** $\boldsymbol{\langle I^2\rangle^{1/2} = \sqrt{\frac{k_B}{L}}}$

Homework find expression for voltage noise

$I = \frac{dQ}{dt}$ Energy $E = \frac{1}{2}LI^2 + \frac{1}{2}\frac{Q^2}{C}$