THERMAL & STATISTICAL PHYSICS
SSP3133

THE PARTITION FUNCTION

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the probability of a system in state s with energy E_s

$$P_s = Ce^{-\beta E_s}$$

Let: χ: a property, having value χ_S when the system in state S

Average value:

$$\overline{\chi} = \sum_s P_S \chi_S = \sum_S Ce^{-\beta E_s} \chi_S$$

-involving large number
-calculation can be cumbersome

Simplified – introduce --- partition function

Normalization: the sum of all of the probabilities must equal 1.

The normalization constant of the probability is 1/Z where Z is called the partition function.

Definition

$$Z = \sum_S e^{-\beta E_S}$$

note: β = 1/kT

The sum over the Boltzmann factors exp(-*βE*)

The probability of a particular state S with energy E_S is given by

$$P_S = \left(\sum_{S'} e^{-\beta E_{S'}} \right)^{-1} e^{-\beta E_S} = Z^{-1} e^{-\beta E_S}$$

If in any given state S, $E_S = E_S(V, N)$

Form 1st law $E_S = E_S(S, V, N)$

Entropy, S is a measure of the number of states, Ω_S

For one certain state s, $\Omega_S = 1$ $S_S = k \ln \Omega_S = k \ln(1) = 0$

-specifying the state, fixed the entropy, $dS = 0$

Pressure $p_s = -\left(\frac{\partial E_S}{\partial V}\right)_N$

1st Law: $dE_s = -p_s dV + \mu_s dN$

Chemical pot. $\mu_s = -\left(\frac{\partial E_S}{\partial N}\right)_V$

Since E is a function of V, N and β changes with T

$$Z\,(T, V, N) = \Sigma\, e^{-\beta E(V,N)}$$

Mean values

$$\bar{\chi} = \sum_{s} P_S \chi_S$$

Internal Energy:

$$\bar{U} = \sum_{s} P_S U_S = Z^{-1} \sum_{S} e^{-\beta U_s} U_S$$

$$= -Z^{-1} \frac{\partial}{\partial \beta} \left(\sum_{S} e^{-\beta U_s} \right) = -Z^{-1} \frac{\partial}{\partial \beta} Z$$

$$= -\frac{\partial}{\partial \beta} \ln\ Z$$

The Z can also be used to determine the fluctuations in the internal energy, σ

$$\overline{U^2} = \sum_S P_S U_S^2$$

$$= Z^{-1} \sum_S e^{-\beta U_S} U_S = Z^{-1} \frac{\partial^2}{\partial \beta^2} \left(\sum_S e^{-\beta U_S} \right)$$

$$= Z^{-1} \frac{\partial^2}{\partial \beta^2} Z$$

The mean squared deviation is

$$\sigma^2 = \overline{(\Delta U)^2} = \overline{U^2} - \overline{U}^2 = Z^{-1} \frac{\partial^2}{\partial \beta^2} Z - \left(\frac{\partial \ln Z}{\partial \beta} \right)^2$$

Work backwards

$$\frac{\partial^2 \ln Z}{\partial\beta^2} = \frac{\partial}{\partial\beta}\left(\frac{\partial \ln Z}{\partial\beta}\right)$$

$$= \frac{\partial}{\partial\beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right)$$

$$= \frac{\partial Z^{-1}}{\partial\beta}\frac{\partial Z}{\partial\beta} + \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2}$$

$$= -\frac{1}{Z^2}\frac{\partial Z}{\partial\beta}\frac{\partial Z}{\partial\beta} + \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2}$$

$$= -\left(\frac{\partial \ln Z}{\partial\beta}\right)^2 + \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2}$$

$$\sigma^2 = \frac{\partial^2 \ln Z}{\partial\beta^2}$$

p_S: pressure of the system in state s

$$p_s = -\left(\frac{\partial E_S}{\partial V}\right)_N$$

$$\overline{p} = \sum_s P_S p_S$$

$$= -Z^{-1}\sum_S e^{-\beta U_S}\left(\frac{\partial U_S}{\partial V}\right)_N$$

$$= \frac{1}{\beta}Z^{-1}\frac{\partial}{\partial V}\left(\sum_S e^{-\beta U_S}\right)_{T,N}$$

$$= \frac{1}{\beta}\frac{\partial}{\partial V}(\ln Z)_{T,V}$$

same calculation for chemical potential

replace P_S with $\mu_s = -\left(\frac{\partial E_S}{\partial N}\right)_V$

$$\overline{\mu} = -\frac{1}{\beta}\frac{\partial}{\partial}(\ln Z)_{T,V}$$

Fluctuations and specific heat

$$\overline{U^2} = Z^{-1}\frac{\partial^2 Z}{\partial \beta^2} = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) = \frac{\partial}{\partial \beta}\left(\frac{\partial \ln Z}{\partial \beta}\right) = \frac{\partial}{\partial \beta}\left(-\overline{U}\right)$$

the heat capacity C_V is defined by

$$C_V = \frac{\partial U}{\partial T}$$

To relate the derivative with respect to *T* to that with respect to β

$$\frac{\partial \overline{U}}{\partial \beta} = \frac{\partial T}{\partial \beta}\frac{\partial \overline{U}}{\partial T} = \frac{\partial (k\beta)^{-1}}{\partial \beta}\frac{\partial \overline{U}}{\partial T} = \frac{1}{k}(-1)\frac{1}{\beta^2}\frac{\partial \overline{U}}{\partial T} = -\frac{1}{k\beta^2}\frac{\partial \overline{U}}{\partial T}$$

$$C_V = \frac{\partial U}{\partial T} = -k\beta^2\frac{\partial \overline{U}}{\partial \beta} = --k\beta^2\left(-\overline{U^2}\right) = k\beta^2\overline{U^2} = k\frac{1}{(kT)^2}\overline{U^2}$$

Fluctuation

$$C_V = \frac{1}{kT^2}\overline{\Delta U^2}$$

-the faster the energy of a system increases with temperature, the greater are the fluctuations in its energy.

-systems that require a lot of energy to increase their temperature (small specific heat) have small energy fluctuations.

Entropy & Helmholtz Free Energy

Z=Z(T, V, N) or Z(β, T, N)

$$d\ln Z = \frac{\partial}{\partial \beta}(\ln Z)_{V,N}\,d\beta + \frac{\partial}{\partial V}(\ln Z)_{T,N}\,dV + \frac{\partial}{\partial N}(\ln Z)_{T,V}\,dN$$

Using

$$\overline{U} = -\frac{\partial}{\partial \beta}(\ln Z)_{V,N}$$

$$\overline{p} = \frac{1}{\beta}\frac{\partial}{\partial V}(\ln Z)_{T,V}$$

$$\overline{\mu} = -\frac{1}{\beta}\frac{\partial}{\partial}(\ln Z)_{T,V}$$

$$d\ln Z = -Ud\beta + \beta pdV - \beta\mu dN$$

$$d \ln Z = -U d\beta + \beta p dV - \beta \mu dN$$

Add d(βU) = Udβ + βdU to both sides

$$d(\ln Z+\beta U) = \beta(dU + pdV - \mu dN)$$

$$= \beta(TdS) = (1/k)\, dS$$

or $$dS = d\left(k \ln Z + \frac{U}{T}\right)$$

or $$S = k \ln Z + \frac{U}{T}$$

or $$U - TS = -kT \ln Z$$

$$U - TS = F = -kT \ln Z$$

F: Helmholtz free energy

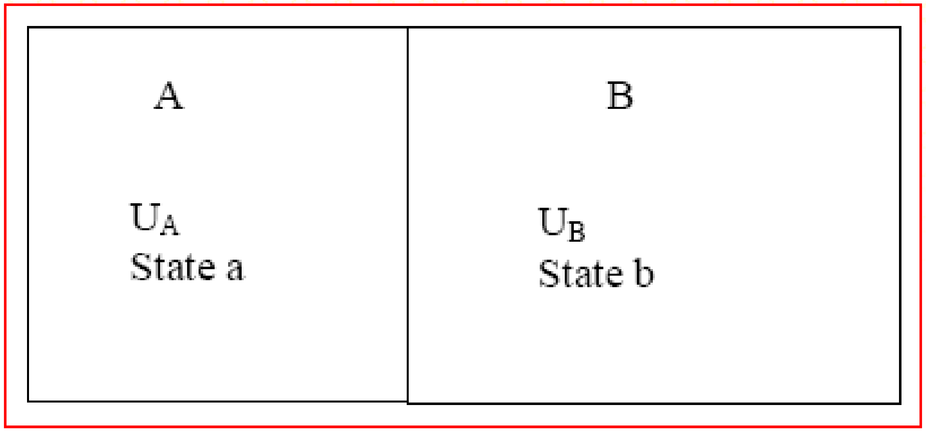
Many applications:

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

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

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

Subsystems & identical subsystem



S: system (in state s)

A, B: subsystems (in state a and b)

The partition function

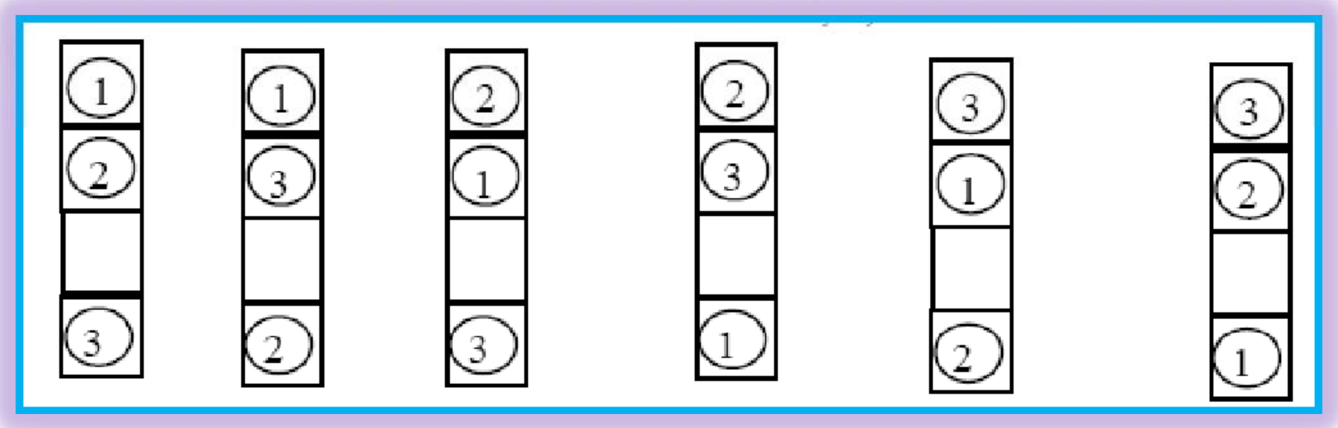
$$Z = \sum_{S} e^{-\beta U_S} = \sum_{a,b} e^{-\beta(U_A + U_B)}$$

$$= \sum_{a} e^{-\beta(U_A)} \sum_{b} e^{-\beta(U_B)} = Z_A Z_B$$

or $Z = Z_A Z_B Z_C \ldots\ldots$

But for identical system

$$\sum_{s} \neq \sum_{a,b,c..}$$



distinguishable: six arrangements ---- six partition functions

identical: one arrangement ------ one partition function for N indistinguishable subsystems

$$\sum_{s} = \frac{1}{N!}\sum_{a,b,c..}$$

$$Z = \sum_{S} e^{-\beta U_S} = \sum_{a,b} e^{-\beta(U_A+U_B+......)} = \frac{1}{N!}\sum_{a,b,c,..} e^{-\beta(U_A+U_B+......)}$$

$$Z = \frac{1}{N!}\sum_{a} e^{-\beta(U_A)}\sum_{b} e^{-\beta(U_B)} ....$$

$$= \frac{1}{N!} Z_A Z_B Z_C ....$$

all subsystems are identical

$Z_A = Z_B = Z_C = \ldots\ldots\ldots$

$$Z = \frac{1}{N!}\zeta^N$$

ζ: Partition function for any of the identical subsystems
-can rewrite

$$Z = \frac{1}{N!}\left(\sum_i e^{-\beta U_i}\right)^N$$

Note:

Show that $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT \ln \frac{\zeta}{N}$

Partition function for a gas

System: N diatomic molecules gas

$$Z = \frac{1}{N!}\zeta^{N}$$

but

$$\zeta = \sum_{a,b,c,\ldots} e^{-\beta(\varepsilon_t+\varepsilon_r+\varepsilon_v+\varepsilon_e+\varepsilon_n+\ldots)} = \ldots\ldots = \zeta_a \zeta_b \zeta_c \ldots\ldots$$

let energy ground state $\varepsilon_0 = 0$ & ε_e is positive

$$\boxed{\zeta = \sum_i e^{-\beta(\varepsilon_i} = e^{-0} + e^{-\varepsilon_{e1}} + e^{-\varepsilon_{e2}} + \ldots..}$$

$$\boxed{\text{if } \varepsilon_{e1} >> kT}$$

$$\boxed{\zeta = \sum_i e^{-\beta(\varepsilon_i)} = 1 + 0 + 0 + \ldots} \quad \boxed{= 1}$$

The End

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