Combining the results of the foregoing discussion, we arrive at the following recipe for deriving thermodynamics from a statistical beginning: determine, for the macrostate (N, V, E) of the given system, the number of all possible microstates accessible to the system; call this number $\Omega(N, V, E)$. Then, the entropy of the system in that state follows from the fundamental formula

$$S(N, V, E) = k \ln \Omega(N, V, E)$$

while the leading *intensive* parameters, viz. temperature, pressure and chemical potential, are given by

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T} \Rightarrow T = \left(\frac{\partial E}{\partial S}\right)_{N,V}$$

$$\left(\frac{\partial S}{\partial V}\right)_{N,E} = \frac{P}{T} \Rightarrow \mathbf{P} = -\left(\frac{\partial E}{\partial V}\right)_{N,S}$$

$$\left(\frac{\partial S}{\partial N}\right)_{V,E} = -\frac{\mu}{T} \Rightarrow \boldsymbol{\mu} = \left(\frac{\partial E}{\partial N}\right)_{V,S}$$

$\mathbf{dE = dQ - PdV + \mu dN}$

$\mathbf{dQ = TdS}$

$\Rightarrow \mathbf{dE = TdS - PdV + \mu dN}$

$$\left.\frac{\partial S}{\partial E}\right|_{V,N} = \frac{1}{T} \quad \& \quad \left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{P}{T} \quad \& \quad \left.\frac{\partial S}{\partial N}\right|_{E,V} = -\frac{\mu}{T}$$

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \Rightarrow T = \left(\frac{\partial E}{\partial S}\right)_{N,V}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \Rightarrow$$

$$P = \left(\frac{\partial S}{\partial V}\right)_{N,E} \Big/ \left(\frac{\partial S}{\partial E}\right)_{N,V} = -\left(\frac{\partial E}{\partial V}\right)_{N,S}$$

$$\mu = -\left(\frac{\partial S}{\partial N}\right)_{V,E} \Big/ \left(\frac{\partial S}{\partial E}\right)_{N,V} = \left(\frac{\partial E}{\partial N}\right)_{V,S}$$

The evaluation of P, μ and T from these formulae indeed requires that the energy E be expressed as a function of the quantities N, V and S.

$$E = f(N, V, S)$$

This should, in principle, be possible once S is known as a function of N, V and E.

$$S = f(N, V, E)$$

The rest of the thermodynamics follows straightforwardly.

For instance, the **Helmholtz free energy A, the Gibbs free energy G and the enthalpy H are given by**

A = E - TS

G = E - TS + PV

H = E + PV

تمرین: تحت چه شرایطی می توان انرژی درونی (آنتروپی) را برا یافتن حالت تعادل ترمودینامیکی یک دستگاه کمینه (بیشینه) کرد؟ (راهنمایی: به کتاب رایشل مراجعه نمایید.)

E ⟹ (V, S, N)

H ⟹ (P, S, N)

A ⟹ (V, T, N)

G ⟹ (P, T, N)

H = E + PV

dH = dE + PdV + VdP

dE = TdS – PdV + μdN ⊕

dH = TdS + VdP + μdN

dE = TdS – PdV + μdN (S, V, N)

dH = TdS + VdP + μdN (S, P, N)

A = E - TS

dA = dE - TdS - SdT

dE = TdS – PdV + μdN ⊕

dA = -SdT - PdV + μdN

dE = TdS – PdV + μdN (S, V, N)

dA = -SdT - PdV + μdN (T, V, N)

G = E – TS +PV

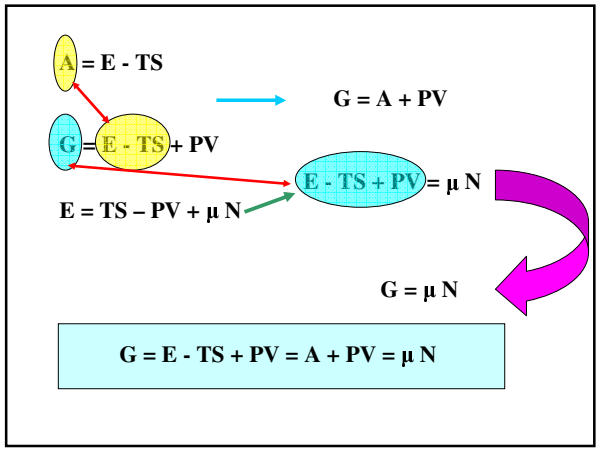
dG = dE - TdS – SdT +PdV +VdP

dE = TdS – PdV + μdN ⊕

dG = -SdT + VdP + μdN

dE = TdS – PdV + μdN (S, V, N)

dG = -SdT + VdP + μdN (T, P, N)



تمرین: معادله اصلی ترمودینامیک را به دست آورید. (راهنمایی: به کتاب رایشل مراجعه نمایید.)

$$E = TS - PV + \mu N$$

$H=E+PV$

$G=E-TS+PV$

$H=G+TS$

The specific heat at constant volume, Cv, and the one at constant pressure, Cp, would be given by

$$C_V = dQ/dT)_{N,V}$$

$$dE = dQ - PdV + \mu dN$$

$$C_V = dQ/dT)_{N,V} = dE/dT)_{N,V}$$

$$dE = TdS - PdV + \mu dN$$

$$C_V = dQ/dT)_{N,V} = TdS/dT)_{N,V}$$

$$C_P = dQ/dT)_{N,P}$$

$$dE = dQ - PdV + \mu dN$$

$$dE = dQ - PdV + \mu dN - d(PV) + PdV + VdP$$

$$dE + dPV = dQ + VdP + \mu dN$$

$$d(E + PV) = dQ + VdP + \mu dN$$

$$dH = dQ + VdP + \mu dN$$

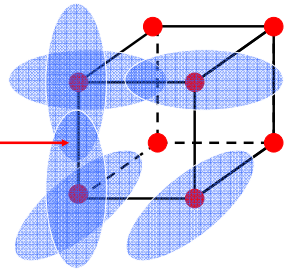
$$C_P = dQ/dT)_{N,P} = dH/dT)_{N,P}$$

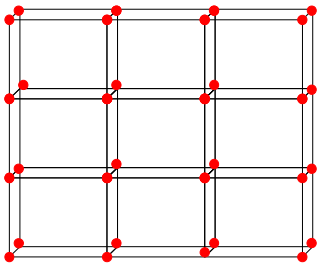
$C_V = TdS/dT)_{N,V}$ $\qquad$ $C_P = dH/dT)_{N,P}$

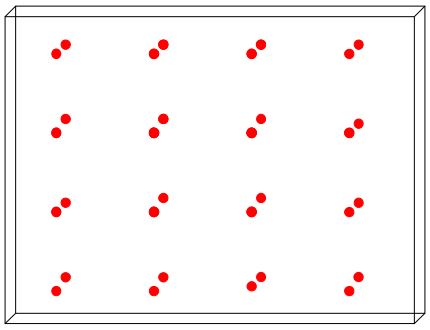
The classical ideal gas

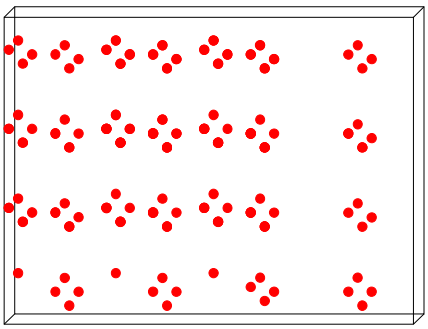
$H\Psi = E\Psi$

$H = T + V$









To illustrate the approach developed in the preceding sections, we shall now derive the various thermodynamic properties of a classical ideal gas composed of monatomic molecules.

The main reason why we choose this highly specialized system for consideration is that it affords

an explicit, though asymptotic, evaluation of the number Ω(N, V, E).

This example becomes all the more instructive when we find that its study enables us, in a most straightforward manner,

to identify the Boltzmann constant κ in terms of other physical constants; R = k N_A.

Moreover, the behavior of this system serves as a useful reference with which the behavior of other physical systems, especially real gases (with or without quantum effects), can be compared. And, indeed, in the limit of high temperatures and low densities the ideal-gas behavior becomes typical of most real systems.

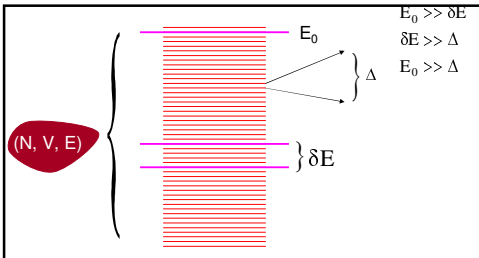
Before undertaking a detailed study of this case it appears worth while to make a remark which applies to all classical systems composed of non-interacting parti- particles, irrespective of the internal structure of the particles.

This remark is related to the explicit dependence of the number Ω(N, V, E) on V and hence to the equation of state of these systems.

Now, **if there do not exist any spatial correlations** among the particles, i.e. if the probability of any one of them being found in a particular region of the available space is completely independent of the location of the other particles, then **the total number of ways in which the N particles can be spatially distributed in the system will be simply equal to the product of the numbers of ways in which the individual particles can be accommodated in the same space independently of one another.**

With N and E fixed, each of these numbers will be directly **proportional to V**, the volume of the container; accordingly, the total number of ways will be directly proportional to the Nth power of V:

$$\Omega (N, E, V) \propto V^N.$$



Ω (E) = E + δE , E تعداد حالتهایی با انرژی بین

E_0= انرژی کل

$\Omega(E) \propto \delta E$

$\Omega(E) = \rho(E)\,\delta E$

Density Of States (DOS)

$\Omega(E) =$ $E + \delta E$, E **تعداد حالتهایی با انرژی بین**

$\Phi(E) =$ **تعداد حالتهایی که انرژی آنها کمتر از** E **است**

$\Phi(E + \delta E) =$ **تعداد حالتهایی که انرژی آنها کمتر از** $E+\delta E$ **است**

$$\Phi(E+\delta E) - \Phi(E) = \Omega(E) = \rho(E)\delta E$$

$$\Phi(E+\delta E) - \Phi(E) = \frac{d\Phi}{dE}\delta E = \rho(E)\delta E \Rightarrow \rho(E) = \frac{d\Phi(E)}{dE}$$

$$E = \frac{\hbar^2 K^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mL^2}$$

$\Phi(E) = ?$

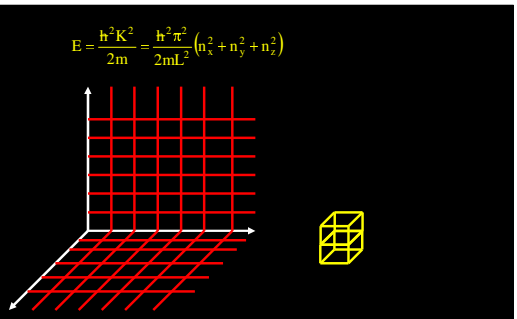
$\Phi(E) = n$

$$n = \frac{L}{\pi\hbar}(2mE)^{1/2} = \Phi(E)$$

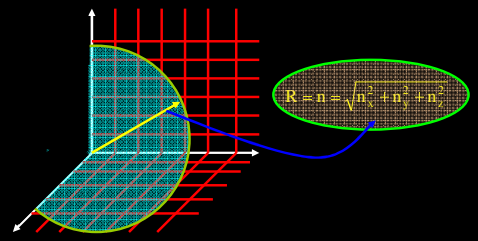
$$\rho(E) = \frac{d\Phi(E)}{dE} = \frac{L}{2\pi\hbar}(2m)^{1/2}E^{-\frac{1}{2}}$$

$$\Omega(E) = \rho(E)\delta E = \frac{L}{2\pi\hbar}(2m)^{1/2}E^{-\frac{1}{2}}\delta E$$

$\Omega(E) \propto L$



$$E = \frac{\hbar^2 K^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$



$$\phi(E) = \frac{1}{8}\times\frac{4}{3}\pi\left(\frac{2mL^2E}{\pi^2\hbar^2}\right)^{3/2} = \frac{\pi}{6}\left(\frac{2mV^{2/3}E}{\pi^2\hbar^2}\right)^{3/2} \qquad ;V = L^3$$

$$E = \frac{\hbar^2 K^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$R = n = \sqrt{n_x^2 + n_y^2 + n_z^2} = \left(\frac{L}{\pi\hbar}\right)(2mE)^{1/2}$$

$$\phi(E) = \frac{1}{8}\times\frac{4}{3}\pi\left(\frac{2mL^2E}{\pi^2\hbar^2}\right)^{3/2} = \frac{\pi}{6}\left(\frac{2mV^{2/3}E}{\pi^2\hbar^2}\right)^{3/2} \qquad ;V = L^3$$

$$\rho(E) = \frac{d\phi(E)}{dE} = \left(\frac{2m\hbar^{-2}V^{2/3}}{\pi^2}\right)^{3/2}\frac{3}{2}E^{1/2}$$

$$\Omega(E) = \rho(E)\delta E = \left(\frac{2m\hbar^{-2}V^{2/3}}{\pi^2}\right)^{3/2}\frac{3}{2}E^{1/2}$$

$\Omega(E) \propto V$

$\Omega(N,V,E) \propto V^N$

$S = k\mathrm{Ln}\Omega(N,V,E)$

$S \propto k\mathrm{Ln}V^N = Nk\mathrm{Ln}V$

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

$$\frac{P}{T} = Nk\frac{1}{V}$$

$PV = NkT = nN_Ak T$

$PV = nRT$ $\Rightarrow$ $k = \frac{R}{N_A}$

For deriving other thermodynamic properties of this system, we require a detailed knowledge of the way Ω depends on the parameters N, V and E.

The problem essentially reduces to determining the total number of ways in which eqns $E = \Sigma n_i E_i$ and $N = \Sigma n_i$ can be mutually satisfied. In other words, we have to determine the total number of (independent) ways of satisfying the equation

$$E = \sum_{r=1}^{3N} \varepsilon_r$$

where the ε_r's are the energies associated with the various degrees of freedom of the N particles.

$$\varepsilon(n_x, n_y, n_z) = \frac{\hbar^2\pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$= \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$n_x^2 + n_y^2 + n_z^2 = \frac{8mL^2}{h^2}\varepsilon(n_x, n_y, n_z)$$

$$= \varepsilon^*_{n_x, n_y, n_z}$$

$$\sum_{n_x}\sum_{n_y}\sum_{n_z} \varepsilon^*_{n_x, n_y, n_z} = \sum_{r=1}^{3N} \varepsilon^*_r$$

$$\sum_{r=1}^{3N} n_r^2 = \frac{8mV^{2/3}}{h^2}\sum_{r=1}^{3N}\varepsilon_r = \frac{8mV^{2/3}}{h^2}E = \frac{8m}{h^2}\left(V^{2/3}E\right)\sum_{r=1}^{3N}\varepsilon_r^* = E^*$$

An important result follows straightforwardly from eqn.,

$$\sum_{r=1}^{3N} n_r^2 = \frac{8mV^{2/3}}{h^2}\sum_{r=1}^{3N}\varepsilon_r = \frac{8mV^{2/3}}{h^2}E = \frac{8m}{h^2}\left(V^{2/3}E\right)\sum_{r=1}^{3N}\varepsilon_r^* = E^*$$

even before the number Ω(N, E, V) is explicitly evaluated. From the nature of the expression appearing on the right-hand side of this equation we conclude that the volume V and the energy E of the system enter into the expression for Ω in the form of the combination ($V^{2/3}E$). Consequently,

$$S(N, V, E) \equiv S(N, V^{2/3}E)$$

Hence, for the constancy of S and N, which defines a reversible adiabatic process,

$$V^{2/3}E = \text{const.}$$

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

$$= -\left(-\frac{2}{3}\text{const.}V^{-5/3}\right) =$$

$$= \frac{2}{3}V^{2/3}EV^{-5/3}$$

$$= \frac{2}{3}\frac{E}{V} \Rightarrow PV = \frac{2}{3}E \Rightarrow E = \frac{3}{2}nRT$$

that is, the pressure of a system of nonrelativistic, non-interacting particles is precisely equal to two-thirds of its energy density. It should be noted here that, since an explicit computation of the number Ω has not yet been done, results $V^{2/3}E$ = const. and E=3/2nRT hold for quantum as well as classical statistics.

$$E = \frac{3}{2}PV = \frac{3}{2}nRT = \frac{3}{2}NkT$$

$$V^{\frac{2}{3}}E = \text{const.} \Rightarrow V^{\frac{2}{3}}\frac{3}{2}PV = \text{const.}$$

$$PV^{\frac{5}{3}} = \text{const.} \equiv PV^{\gamma} = \text{const.}$$

$$\gamma = \frac{C_P}{C_V} = ?$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} = \left.\frac{\partial(3/2nRT)}{\partial T}\right)_{N,V} = 3/2nR = 3/2NK$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{N,P} = \left.\frac{\partial(E+PV)}{\partial T}\right)_{N,P} = \left.\frac{\partial(3/2nRT + nRT)}{\partial T}\right)_{N,P} = 5/2nR = 5/2NK$$

$$\gamma = \frac{C_P}{C_V} = \frac{5/2}{3/2} = \frac{5}{3}$$ ☺

$$V^{\frac{2}{3}}E = \text{const.} \Rightarrow V^{\frac{2}{3}}\frac{3}{2}PV = \text{const.}$$

$$V^{\frac{2}{3}}\frac{3}{2}nRT = \text{const.}$$

$$V^{\frac{2}{3}}T = \text{const.}$$

$$TV^{\gamma-1} = \text{const.}$$ ☺

$$\gamma - 1 = 5/3 - 1 = 2/3$$