
Thermodynamics

Statistical Thermodynamics – II

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Equipartition Theorem

The average energy of a particle per independent component of motion is $\frac{1}{2}kT$

$$\varepsilon = \varepsilon' + \varepsilon'' + \varepsilon''' + \dots \quad Z = \sum e^{-\varepsilon/kT} = \sum e^{-(\varepsilon' + \varepsilon'' + \varepsilon''' + \dots)/kT} = Z' Z'' Z''' \dots$$

$$U = NkT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V \quad \langle \varepsilon \rangle = \frac{U}{N} = - \frac{\partial \ln Z}{\partial \beta}$$

translational kinetic energy : $\frac{1}{2}mv^2$

rotational kinetic energy : $\frac{1}{2}I\omega^2$

vibrational energy : $\frac{1}{2}mv^2 + \frac{1}{2}kx^2$

kinetic energy for each independent component of motion has a form of $b_i p_i^2$

$$\varepsilon = b_1 p_1^2 + b_2 p_2^2 + \dots + b_f p_f^2 \quad P = \int_0^\infty e^{-\beta b_1 p_1^2} dp_1 \int_0^\infty e^{-\beta b_2 p_2^2} dp_2 \dots \int_0^\infty e^{-\beta b_f p_f^2} dp_f$$

$$y_i = \beta^{1/2} p_i \quad \int_0^\infty e^{-\beta b_i p_i^2} dp_i = \beta^{-1/2} \int_0^\infty e^{-b_i y_i^2} dy_i = \beta^{-1/2} K_i$$

$$Z = \beta^{-1/2} K_1 \cdot \beta^{-1/2} K_2 \dots \beta^{-1/2} K_f = \beta^{-f/2} K_1 K_2 \dots K_f$$



Equipartition Theorem

The average energy of a particle per independent component of motion is $\frac{1}{2}kT$

$$Z = \beta^{-f/2} K_1 K_2 \cdots K_f \qquad \langle \varepsilon \rangle = -\frac{\partial \ln P}{\partial \beta} = \frac{f}{2\beta} = \frac{f}{2} kT$$

※ for a monoatomic ideal gas : $u = \frac{3}{2}RT$

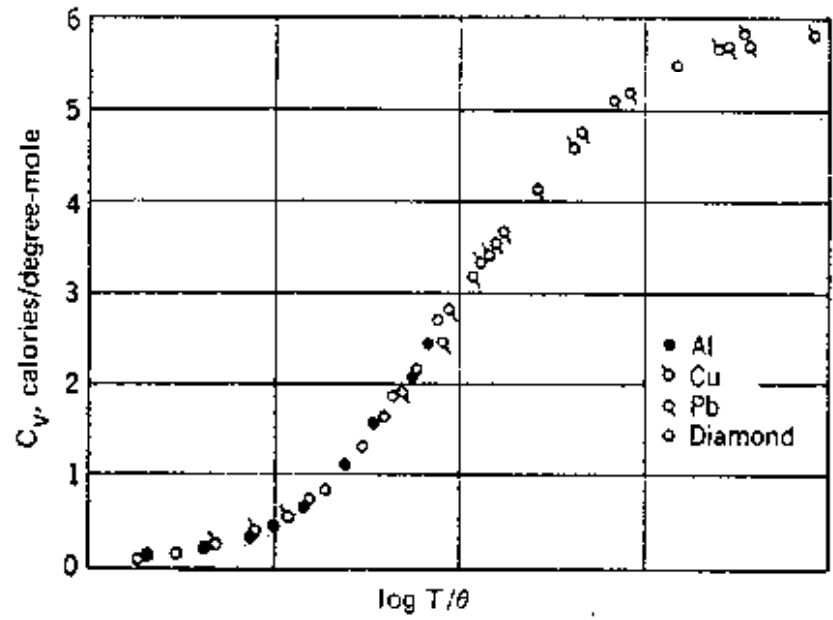
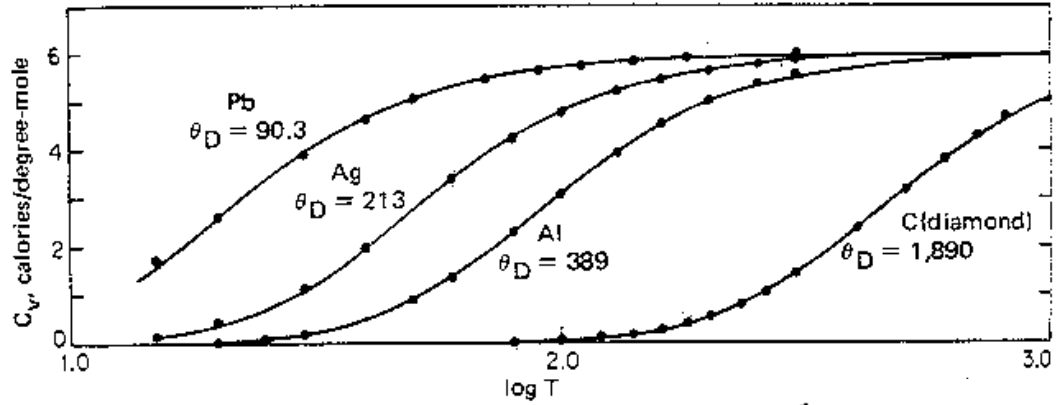
for diatomic gases : $u = \frac{5}{2}RT$

for polyatomic molecules which are soft and vibrate easily
with many frequencies, say, q : $u = (3 + q)RT$

※ for liquids and solids, the equipartition principle does not work



Einstein and Debye Model for Heat Capacity – Background



Einstein and Debye Model for Heat Capacity – Concept

3N independent (weakly interacting) but distinguishable simple harmonic oscillators.

$$\varepsilon_i = \left(i + \frac{1}{2}\right) h\nu$$

$$P = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}} \quad \ln P = -\frac{1}{2} \frac{h\nu}{kT} - \ln(1 - e^{-h\nu/kT})$$

for N simple harmonic vibrators

$$U = NkT^2 \left(\frac{\partial \ln P}{\partial T} \right)_\nu = N \left(\frac{1}{2} h\nu + \frac{h\nu}{e^{h\nu/kT} - 1} \right)$$

average energy per vibrator

$$\langle \varepsilon \rangle = \frac{h\nu}{2} + \frac{h\nu}{e^{h\nu/kT} - 1}$$



Einstein and Debye Model for Heat Capacity – number density

Let dN_ν be the number of oscillators whose frequency lies between ν and $\nu + d\nu$

$$dN_\nu = g(\nu) d\nu$$

where $g(\nu)$, the number of vibrators per unit frequency band, satisfy the condition

$$\int dN_\nu = \int g(\nu) d\nu = 3N$$

The energy of N particles of the crystal

$$U = \int \langle \varepsilon \rangle dN_\nu = \int \left(\frac{h\nu}{2} + \frac{h\nu}{e^{h\nu/kT} - 1} \right) g(\nu) d\nu$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \int \frac{k(h\nu/kT)^2 e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} g(\nu) d\nu$$



Einstein and Debye Model for Heat Capacity – Einstein

All the $3N$ equivalent harmonic oscillators have the same frequency ν_E

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \int \frac{k(h\nu/kT)^2 e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} g(\nu) d\nu$$

$$C_V = 3N \frac{k(h\nu_E/kT)^2 e^{h\nu_E/kT}}{(e^{h\nu_E/kT} - 1)^2}$$

Defining Einstein characteristic temperature

$$\theta_E = \frac{h\nu_E}{k}$$

$$\frac{c_V}{3R} = \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}$$



Einstein and Debye Model for Heat Capacity – Debye

A crystal is a continuous medium supporting standing longitudinal and transverse waves

$$g(\nu) = \frac{9N}{v_m^3} \nu^2 \quad C_V = \left(\frac{\partial U}{\partial T} \right)_V = \int \frac{k(h\nu/kT)^2 e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} g(\nu) d\nu$$

$$\frac{C_V}{3Nk} = \int_0^{\nu_m} \frac{(3\nu^2 / v_m^3)(h\nu/kT)^2 e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} d\nu$$

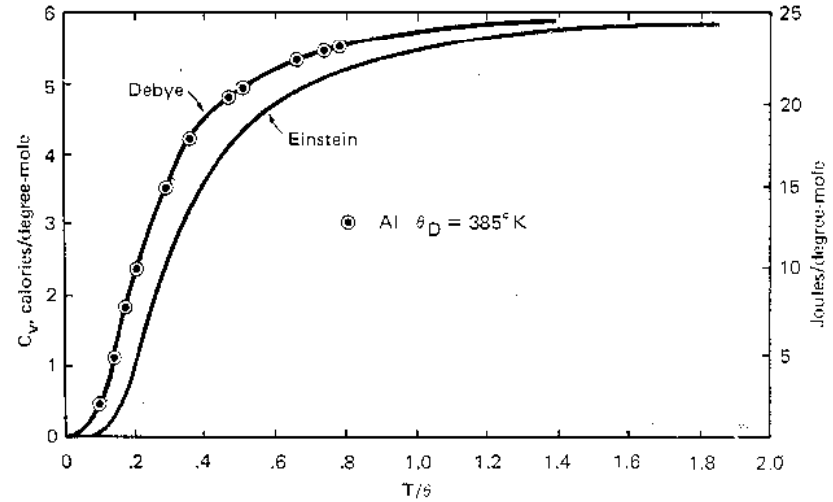
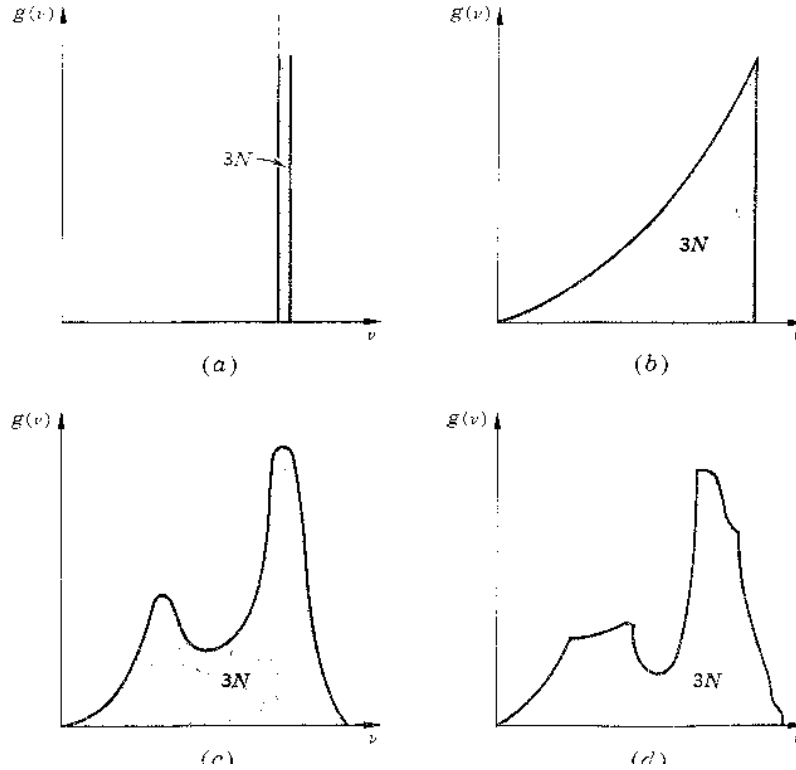
set

$$x = \frac{h\nu}{kT} \quad x_m = \frac{h\nu_m}{kT} = \frac{\Theta}{T}$$

$$\frac{C_V}{3R} = \frac{3}{(\Theta/T)^3} \int_0^{\Theta/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$



Einstein and Debye Model for Heat Capacity – Comparison

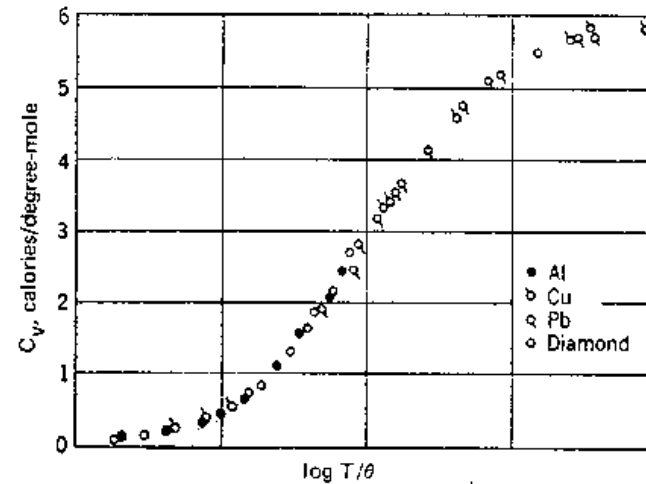
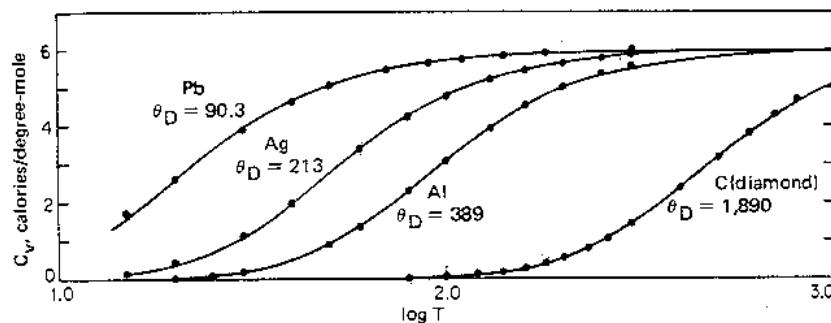


Einstein and Debye Model for Heat Capacity – More about Debye

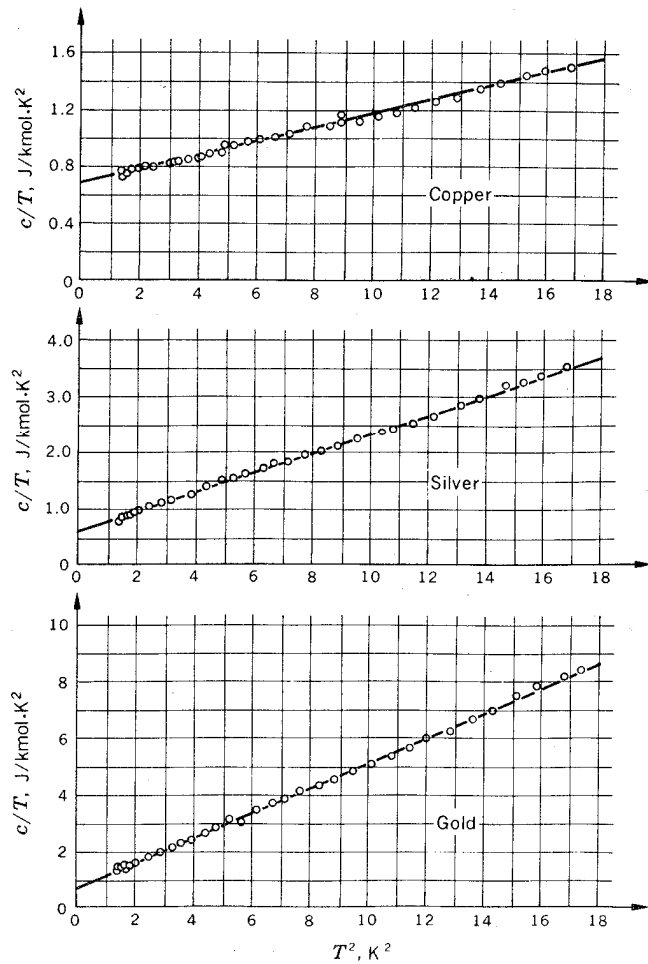
Behavior of $\frac{c_V}{3R} = \frac{3}{(\Theta/T)^3} \int_0^{\Theta/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$ at $T \rightarrow \infty$ and $T \rightarrow 0$

at $T \rightarrow \infty$ $\frac{x^4 e^x}{(e^x - 1)^2} \rightarrow x^2$ $c_V = 3R$

at $T \rightarrow 0$ $\frac{c_V}{3R} = \frac{4\pi^4}{5} \left(\frac{T}{\Theta}\right)^3$: Debye's T^3 law



Einstein and Debye Model for Heat Capacity – More about Cp



$$c_e = \gamma' \cdot T$$

for $T \ll T_F$



Effusion: Langmuir Equation

Question: The rate at which particles strike a unit surface of a container per unit time, given the pressure and temperature of the gas

Application:

- 1. Estimate of the time needed for a totally clean surface to be covered with a monolayer of atoms or molecules, assuming that all the molecules that hit the surface stick to it**
- 2. Calculate how many atoms will escape from a small hole in a vessel per unit time, given the area of hole (measure of vapor pressure)**
- 3. How many particles may evaporate from a surface per unit time**



Maxwell Distribution of Speed in Dilute Gases

$$n(\varepsilon) = \frac{N}{Z} g(\varepsilon) e^{-\varepsilon/kT} \quad \varepsilon = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) = \frac{h^2}{8mL^2} r^2$$

$$g(\varepsilon)d\varepsilon = \frac{1}{8} 4\pi r^2 dr = \frac{2\pi V (2m)^{3/2}}{h^3} \varepsilon^{1/2} d\varepsilon$$

$$n(\varepsilon)d\varepsilon = 2\pi N \left(\frac{1}{\pi kT} \right)^{3/2} \varepsilon^{1/2} \exp\left(-\frac{\varepsilon}{kT}\right) d\varepsilon$$

$$Z = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2}$$

$$n(v)dv = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv$$

$$\varepsilon = \frac{1}{2} mv^2$$

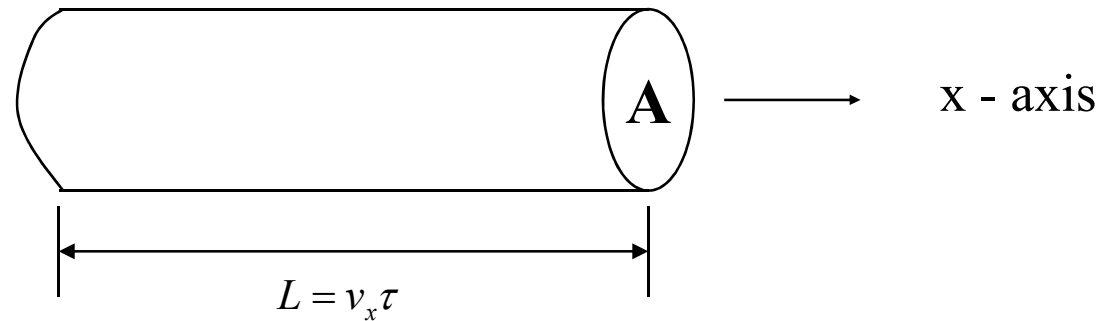
$$\langle v \rangle = \frac{\int_0^\infty v n(v) dv}{N} = \left(\frac{8kT}{\pi m} \right)^{1/2}$$

$$\langle v^2 \rangle = \frac{3kT}{m}$$

$$v^* = \left(\frac{2kT}{m} \right)^{1/2}$$



Effusion: Langmuir Equation



Number of atoms N^* that collide with side walls within a time τ

$$N^* = \sum_i v_{x,i} \tau A \frac{N}{V} \frac{1}{2} [\textit{probability of } v_{x,i}]$$

$$N^* = \sum_i v_{x,i} \tau A \frac{N}{V} \frac{1}{2} \left[\frac{\exp\left(-\frac{h^2}{8mV^{2/3}kT} i^2\right)}{Z} \right]$$



Effusion: Langmuir Equation

$$N^* = \sum_i v_{x,i} \tau A \frac{N}{V} \frac{1}{2} \left[\frac{\exp\left(-\frac{h^2}{8mV^{2/3}kT} i^2\right)}{Z} \right] \quad \gamma^2 \equiv \frac{h^2}{8mV^{2/3}kT}$$

$$v_{x,i} = \left(\frac{2kT}{m}\right)^{1/2} \cdot \gamma \cdot i \quad Z = V \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \quad Z_x = V^{1/3} \left(\frac{2\pi mkT}{h^2}\right)^{1/2}$$

$$\frac{N^*}{A\tau} = \frac{1}{2} \frac{N}{VZ} \gamma \left(\frac{2kT}{m}\right)^{1/2} \int_0^\infty i \exp(-\gamma^2 i^2) di \quad \int_0^\infty i \exp(-\gamma^2 i^2) di = \frac{1}{2\gamma^2}$$

$$\frac{N^*}{A\tau} = \frac{NkT}{V} \left(\frac{1}{2\pi mkT}\right)^{1/2} \quad \frac{N^*}{A\tau} = \frac{P}{(2\pi mkT)^{1/2}}$$



Effusion: Langmuir Equation

$$\frac{N^*}{A\tau} = \frac{P}{(2\pi mkT)^{1/2}} \quad \frac{N^*}{A\tau} (\text{cm}^{-2} \text{sec}^{-1}) = \frac{P(\text{atm}) \times 101325}{\left[2\pi \frac{M \times 10^{-3}}{6.022 \times 10^{23}} \times 1.38 \times 10^{-23} T \right]^{1/2}} \times 10^{-4}$$

Assume 10^{15} atoms per cm^2 in the surface monolayer.

For O_2 ($M=32$ g/mol) at 300K and at 10^{-10} atm, about 37sec is necessary for monolayer deposition.

$$\frac{N^*}{A\tau} = 2.72 \times 10^{23} P = \frac{10^{15}}{\tau}$$

To keep the surface clean for 1 hour, the pressure should be 10^{-12} atm.

At equilibrium, rate of evaporation is the same as the rate of deposition.

$$\frac{N^{evapor}}{A\tau} = \frac{P^{equil}}{(2\pi mkT)^{1/2}}$$

ex) for liquid Al in vacuum at 1250 K,
 mass loss due to a hole of $2 \times 10^{-3} \text{ cm}^2$
 $\rightarrow 1.7 \times 10^{-9} \text{ g/s}$
 \rightarrow Knudsen effusion method

$$P^{equil} = \frac{N^{evapor}}{A\tau} (2\pi mkT)^{1/2} = 1.30 \times 10^{-7} \text{ atm}$$



Effusion: Langmuir Equation

Knudsen effusion method:
(valid for **Knudsen flow**)

$$P^{equil} = \frac{N^{evapor}}{A\tau} (2\pi mkT)^{1/2} \quad \frac{P_1}{P_2} = \left[\frac{T_1}{T_2} \right]^{1/2}$$

Mean free path

$$\lambda = \frac{\bar{v}t}{(N/V)\bar{v}t\pi\sigma^2} = \frac{1}{\pi\sigma^2(N/V)} \Rightarrow \frac{1}{\sqrt{2}\pi\sigma^2(N/V)} > a$$

for ideal gas

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 P}$$

ex) O₂ gas (diameter = 3 × 10⁻¹⁰ m) at 300 K

$$\lambda = \frac{(1.38 \times 10^{-23}) \times 300}{\sqrt{2}\pi(3 \times 10^{-10})^2 (P_{(atm)} \times 1.103 \times 10^5)} = \frac{1.02 \times 10^{-7}}{P_{(atm)}} \text{ (meter)}$$

at 1 atm, λ = 10⁻⁷ m

at 10⁻⁹ atm, λ = 100 m

λ / a > 1 Knudsen flow

λ / a < 0.01 Viscous flow



Diffusion in Gases

$$J_m = -D \left(\frac{\partial C}{\partial x} \right)$$

$$C^* = C_o^* + \left(\frac{\partial C}{\partial x} \right) dx$$

$$N = \frac{1}{6} \langle v \rangle C_{x+\lambda}^*$$

$$J = \vec{N} - \overleftarrow{N} = -\frac{1}{3} \langle v \rangle \left(\frac{\partial C}{\partial x} \right) \lambda$$

$$D = \frac{1}{3} \langle v \rangle \lambda$$

$$\langle v \rangle = \left(\frac{8kT}{\pi m} \right)^{1/2}$$

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 P}$$

$$D = \frac{2}{3} \left(\frac{k}{\pi} \right)^{3/2} \frac{1}{m^{1/2}} \frac{T^{3/2}}{\sigma^2 P}$$

for $\lambda \ll L$



Flux during PVD – Evaporation (Langmuir) or Diffusion Controlled ?

Consider W evaporation at 2473K onto cold substrate along 3cm path.
in vacuum

$$P^{equil} = 1.23 \times 10^{-10} \text{ atm} \quad \lambda = \frac{kT}{\sqrt{2\pi}\sigma^2 P} = 10^5 \text{ cm}$$
$$J_W = \frac{N^*}{A\tau} = \frac{P}{(2\pi mkT)^{1/2}} = 4.85 \times 10^{16} \text{ atoms} / m^2 \cdot s$$

in 0.1 atm N₂ gas

$$\lambda = 10^{-4} \text{ cm}$$

$$D = \frac{2}{3} \left(\frac{k}{\pi} \right)^{3/2} \frac{1}{m^{1/2}} \frac{T^{3/2}}{\sigma^2 P} = 1.66 \times 10^{-3} \text{ m}^2 / s$$

$$C = \frac{N}{V} = \frac{P}{kT} = 3.6 \times 10^{14} \text{ atom} / m^3$$

$$J_W = -D \frac{\Delta C}{\Delta x} = 2 \times 10^{13} \text{ atoms} / m^2 \cdot s$$



Flux during PVD – General

Langmuir Equation

$$J_W = \frac{N^*}{A\tau} = \frac{P_W}{(2\pi mkT_W)^{1/2}}$$

Diffusion Controlled

$$J_W = -D \frac{\Delta C}{\Delta x} \quad C = \frac{N}{V} = \frac{P}{kT}$$

$$J_W = \frac{P_W}{kT_W \Delta x / D}$$

In General

$$J_W = \frac{P_W}{(2\pi mkT_W)^{1/2} + kT\Delta x / D}$$



Size Distribution of Molecules in Polymer

For a polymer with N_A mers (segment) : N_A (Avogadro number)

X = number of segments in molecules

N_x = number of molecules with size X

N = total number of molecules

n_x = fraction of molecules with size $X = N_x/N$

N_b = number of bonding between segments

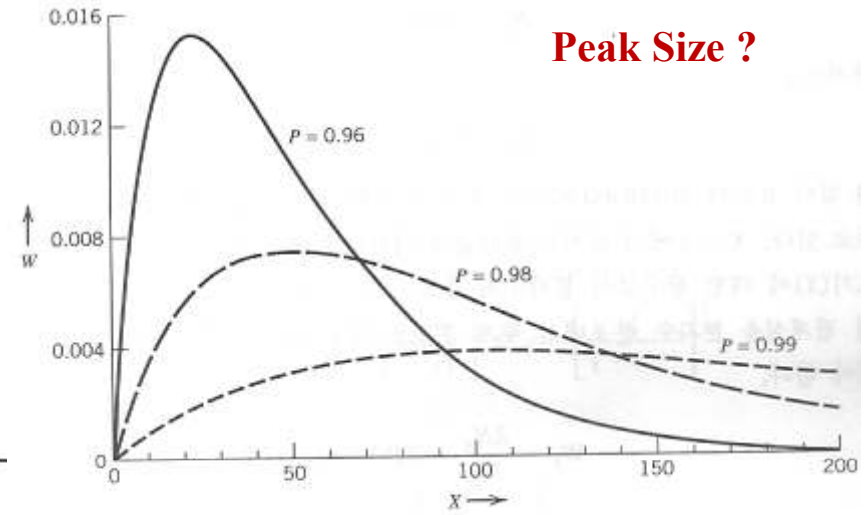
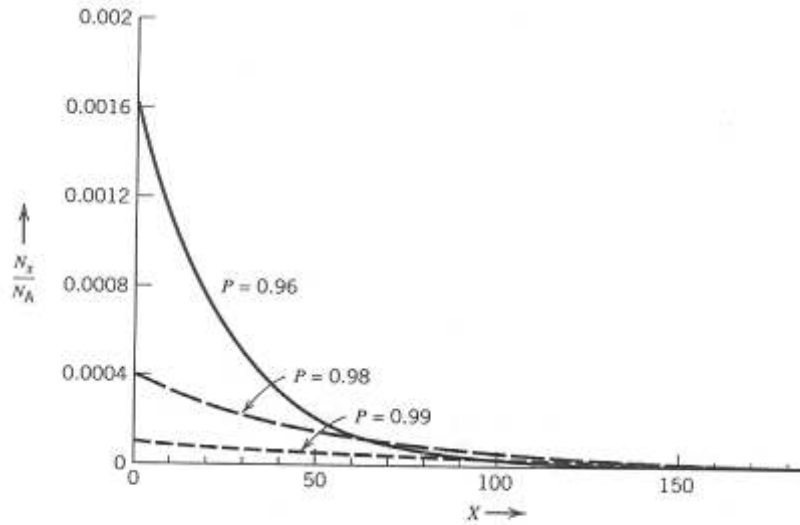
P = 고분자도 (중합도, degree of polymerization) = N_b/N_A

$$N_b = \sum_X (X - 1)N_x$$

$$P = 1 - \frac{N}{N_A}$$



Size Distribution of Molecules in Polymer



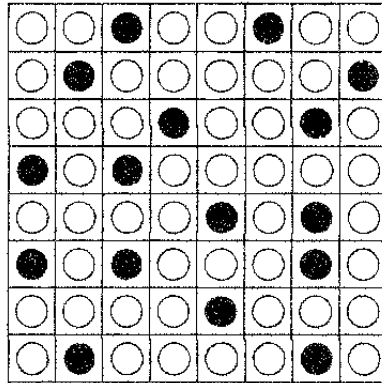
$$\frac{N_A}{N} = \frac{1}{1 - e^{-\lambda}} \quad e^{-\lambda} = 1 - \frac{N}{N_A}$$

$$n_x = \frac{(e^{-\lambda})^x}{e^{-\lambda} / (1 - e^{-\lambda})} = (e^{-\lambda})^{x-1} (1 - e^{-\lambda}) = \left(1 - \frac{N}{N_A}\right)^{x-1} \left(\frac{N}{N_A}\right) = P^{x-1} (1 - P)$$

$$N_x = N_A P^{x-1} (1 - P)^2 \quad W_x = \frac{x N_x}{N_A} = x P^{x-1} (1 - P)^2$$

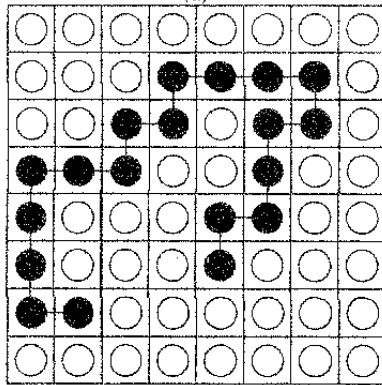


Entropy of Mixing in Polymer Solutions - Flory Huggins Theory



○ Solvent ● Solute

(a)



○ Solvent ● Chain segments of the polymer

(b)

$$\Delta S_M = -R \sum x_i$$

$$N = N_1 + nN_2$$

Consider the number of segments of the (i)

$$w_{i+1} = (N - ni) Z \left(\frac{N - ni}{N} \right)$$

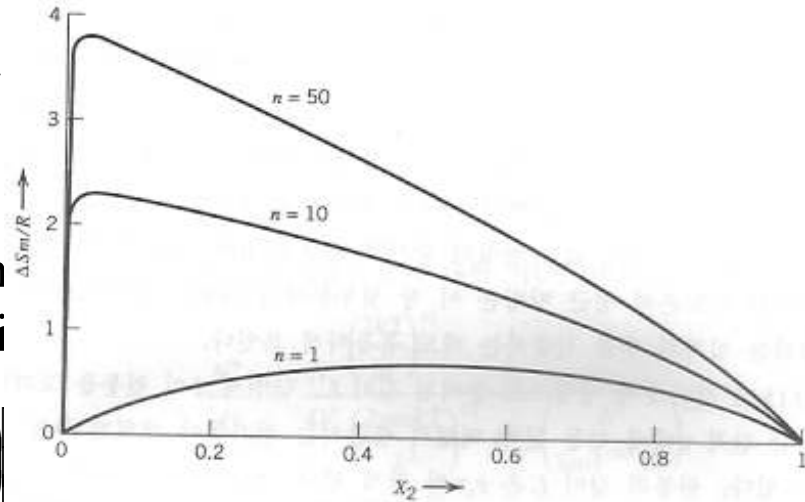
$$\Omega = \frac{1}{N_2!} \prod_{i=1}^{N_2} w_i$$

$$S_c = k \ln \left[\frac{1}{N_2!} \prod_{i=1}^{N_2} w_i \right]$$

$$\frac{S_c}{k} = -N_1 \ln \left(\frac{N_1}{N} \right) - N_2 \ln \left(\frac{nN_2}{N} \right) + N_2 [\ln Z + (n-2) \ln(Z-1) + (1-n) + \ln n]$$

$$\Delta S_M = -k \left(N_1 \ln \left(\frac{N_1}{N} \right) + N_2 \ln \left(\frac{nN_2}{N} \right) \right) = -R \left(x_1 \ln \left(\frac{N_1}{N} \right) + x_2 \ln \left(\frac{nN_2}{N} \right) \right)$$

$$= -R(x_1 \ln \phi_1 + x_2 \ln \phi_2)$$



Elasticity of Rubber – Scope

Ref. – Castellan, Gilbert W., Physical Chemistry 3rd Ed., Benjamin/Cummings, New York, 1983 (Chap. 29)

$$dU = TdS + fdL$$

$$f = \left(\frac{\partial U}{\partial L} \right)_T - T \left(\frac{\partial S}{\partial L} \right)_T = \left(\frac{\partial U}{\partial L} \right)_T + T \left(\frac{\partial f}{\partial T} \right)_L$$

Ideal rubber:

$$\left(\frac{\partial f}{\partial T} \right)_L = \frac{f}{T} \quad \left(\frac{\partial U}{\partial L} \right)_L = 0 \quad f = -T \left(\frac{\partial S}{\partial L} \right)_T$$

Polymer molecules themselves are not stretched, but the degree of alignment is changed.

Position of one end of an N-mer with respect to the position of the other end



Elasticity of Rubber – Statistics of Random Walk

$$P(N_R, N) = \frac{N!}{N_R! N_L!} P_R^{N_R} P_L^{N_L} \quad N_R = \frac{1}{2} \left(N + \frac{x}{l} \right) \quad N_L = \frac{1}{2} \left(N - \frac{x}{l} \right)$$

$$P(x, N) = \frac{N!}{\left(\frac{N+x/l}{2} \right)! \left(\frac{N-x/l}{2} \right)!} \left(\frac{1}{2} \right)^N$$

$$-\ln P(x, N) = \left(\frac{Nl+x}{2l} \right) \ln \left(1 + \frac{x}{Nl} \right) + \left(\frac{Nl-x}{2l} \right) \ln \left(1 - \frac{x}{Nl} \right)$$

$$\ln \left(1 + \frac{x}{Nl} \right) = \frac{x}{Nl} - \frac{1}{2} \left(\frac{x}{Nl} \right)^2$$

$$\ln P(x, N) = -\frac{x^2}{2Nl^2}$$

$$P(x, N) = K \exp \left(-\frac{x^2}{2Nl^2} \right) = \frac{1}{\sqrt{2\pi Nl^2}} \exp \left(-\frac{x^2}{2Nl^2} \right)$$

$$\overline{x^2} = Nl^2$$



Elasticity of Rubber – Statistics of Random Walk

$$P(x, y, z, N) dx dy dz = P\left(x, \frac{N}{3}\right) P\left(y, \frac{N}{3}\right) P\left(z, \frac{N}{3}\right) dx dy dz$$

$$P(x, y, z, N) dx dy dz = \left(2\pi \frac{N}{3} l^2\right)^{-3/2} \exp\left(-\frac{3(x^2 + y^2 + z^2)}{2Nl^2}\right) dx dy dz$$

$$x^2 + y^2 + z^2 = R^2$$

$$dx dy dz = 4\pi R^2 dR$$

$$P(R, N) dR = \left(2\pi \frac{N}{3} l^2\right)^{-3/2} 4\pi R^2 \exp\left(-\frac{3R^2}{2Nl^2}\right) dR$$

$$\overline{R^2} = 4\pi \left(2\pi \frac{N}{3} l^2\right)^{-3/2} \int_0^\infty R^4 \exp\left(-\frac{3R^2}{2Nl^2}\right) dR = Nl^2$$

$$l = \frac{R_{rms}}{N^{1/2}}$$



Elasticity of Rubber – Deformation & Entropy

$$L = L_0 + \Delta L$$

$$\alpha = L / L_0$$

$$\varepsilon = \Delta L / L_0$$

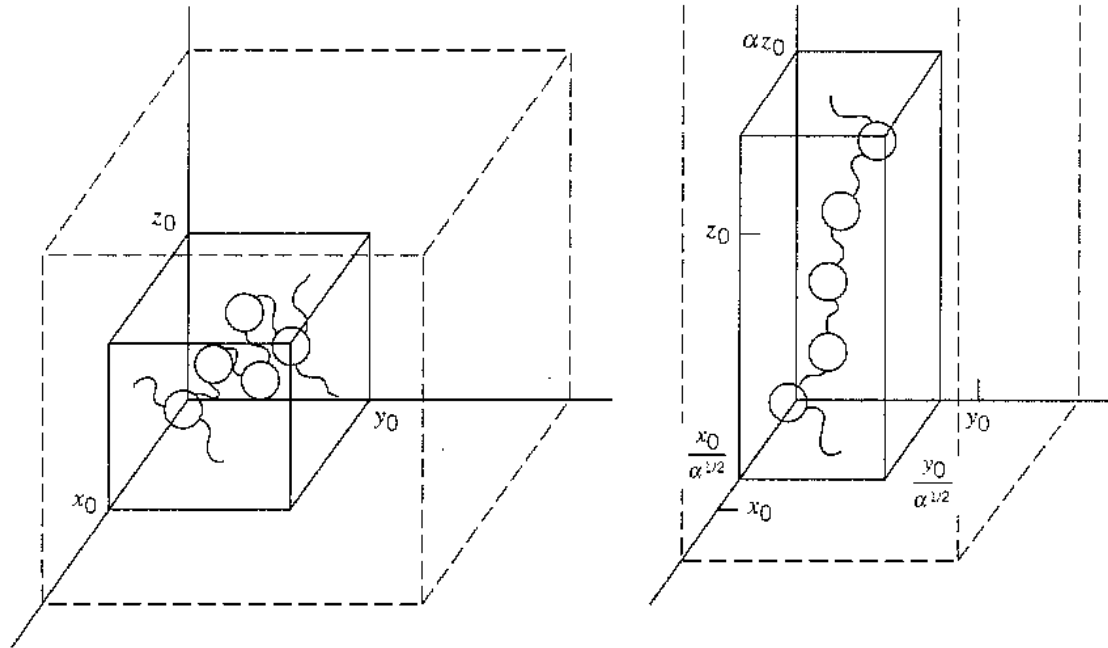
$$\alpha - 1 = \varepsilon$$

When a solid with original dimensions x_0, y_0, z_0 is stretched in the z direction at constant volume

$$z_0 \rightarrow \alpha z_0$$

$$x_0 \rightarrow \frac{1}{\alpha^{1/2}} x_0$$

$$y_0 \rightarrow \frac{1}{\alpha^{1/2}} y_0$$



Elasticity of Rubber – Deformation & Entropy

When a solid with original dimensions x_0, y_0, z_0 is stretched in the z direction at constant volume

$$z_0 \rightarrow \alpha z_0 \qquad x_0 \rightarrow \frac{1}{\alpha^{1/2}} x_0 \qquad y_0 \rightarrow \frac{1}{\alpha^{1/2}} y_0$$

$$P_u dx dy dz = \left(\frac{2}{3} \pi N l^2 \right)^{-3/2} \exp\left(-\frac{3(x^2 + y^2 + z^2)}{2 N l^2} \right) dx dy dz$$

$$P_s dx dy dz = \left(\frac{2}{3} \pi N l^2 \right)^{-3/2} \exp\left(-\frac{3(x^2 / \alpha + y^2 / \alpha + z^2 \alpha^2)}{2 N l^2} \right) dx dy dz$$

Flory, Paul J., Principles of Polymer Chemistry, Cornell University Press, Ithaca, NY, 1960.

$$\Delta S = S_s - S_u = k (\ln \Omega_s - \ln \Omega_u)$$

$$\Delta S_i = -3k \frac{\left[\left(\frac{1}{\alpha} - 1 \right) x^2 + \left(\frac{1}{\alpha} - 1 \right) y^2 + (\alpha^2 - 1) z^2 \right]}{2 N l^2}$$



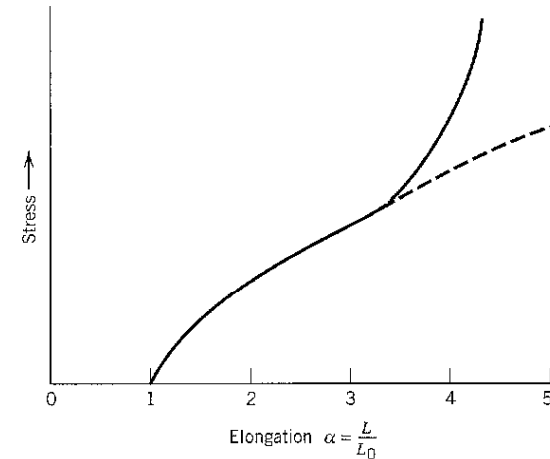
Elasticity of Rubber – Elasticity

$$\Delta S_i = -\frac{3k}{2} \left[\frac{2}{3} \left(\frac{1}{\alpha} - 1 \right) + \frac{1}{3} \alpha^2 - \frac{1}{3} \right]$$

$$\Delta S = -\frac{k\nu}{2} \left[\alpha^2 + \frac{2}{\alpha} - 3 \right]$$

$$f = -T \left(\frac{\partial S}{\partial L} \right)_T = -\frac{T}{L_o} \left(\frac{\partial S}{\partial \alpha} \right)_T = \frac{kT\nu}{L_o} \left(\alpha - \frac{1}{\alpha^2} \right)$$

$$\sigma = \frac{f}{A} = \frac{kT\nu}{V} \left(\alpha - \frac{1}{\alpha^2} \right) = \frac{kT\nu}{V} \left(\frac{L}{L_o} - \left(\frac{L_o}{L} \right)^2 \right)$$



$$d\sigma = \frac{kT\nu}{V} \left(\frac{1}{L_o} + 2 \frac{L_o^2}{L^3} \right) dL = \frac{kT\nu}{V} \left(\frac{L}{L_o} + 2 \frac{L_o^2}{L^2} \right) \frac{dL}{L} = \frac{kT\nu}{V} \left(\alpha + \frac{2}{\alpha^2} \right) \frac{dL}{L} = E \frac{dL}{L}$$

$$E = \frac{kT\nu}{V} \left(\alpha + \frac{2}{\alpha^2} \right) = \frac{RT\rho}{M_c} \left(\alpha + \frac{2}{\alpha^2} \right)$$

$$\frac{\nu}{V} = \frac{\rho N_A}{M_c}$$

