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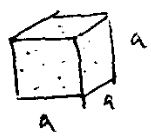
Course 565/665 Lecture Number ______ Date 4/1/03

Lecturer Dr. Silvia Cavagnero Note Taker Eric Fulmer

Last Time

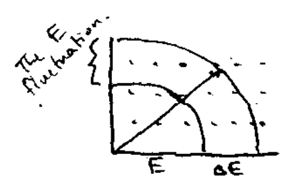
$$M = \frac{1}{8}\left(\frac{4}{3}\pi R^3\right) = \frac{\pi}{6}\left(\frac{8m\varepsilon}{h^2}\right)^{3/2} V$$



$$V = a^3$$

where M is the number of positive integers.

Towards Fluctuations of Energy:



$W(E)\,\Delta E$

↑
# of positive integer points in the shell between the energies E and $(E + \Delta E)$.

$$W(E)\,\Delta E = M(\varepsilon + \Delta\varepsilon) - M(\varepsilon)$$

$$\simeq [redacted] \frac{dM}{d\varepsilon}\,\Delta\varepsilon$$

$$\boxed{W(E)\,\Delta E = \frac{\pi}{4}\left(\frac{8m}{h^2}\right)^{3/2} \cdot V\,\varepsilon^{1/2} \cdot \Delta E}$$

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Example Ar ensemble of particles in gaseous state

$m = 40\ g/mol = 6.64 \times 10^{-26}\ kg/atom$

$T = 300\ K$

$\varepsilon = \frac{3}{2} kT = \frac{3}{2}(1.38 \times 10^{-23}\ J/K)(300\ K)$

$= 6.21 \times 10^{-21}\ J$

$\Delta\varepsilon = 0.01\ \varepsilon$ — i.e. 1% E fluctuations.

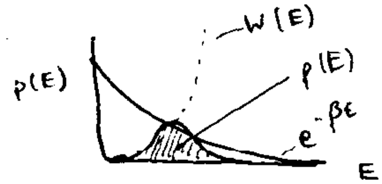
$$W(E)\,\Delta E = \frac{\pi}{4}\left(\frac{8 \times 6.64 \times 10^{-26}\ kg/atom}{(6.626 \times 10^{-34}\ Js)^2}\right) \times (10^{-2}\ m)^2$$

$$\times\ (6.21 \times 10^{-21}\ J)^{3/2}\ (0.01) = 5.11 \times 10^{24}\ \text{states}$$

Conclude: Even a small E fluctuation (1%) gives a large variation in the density of states. ($W(E)\,\Delta E$).

Energy fluctuations

$$p(E) = \frac{W(E)\, e^{-\beta\varepsilon}}{Q}$$



p(E) is maximized where both W(E) and $e^{-\beta\varepsilon}$ are similar in magnitude

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The shape of $p(E)$ is well approximated to be Gaussian.

$\langle E \rangle = U$

$$\ln p(E) = \ln p(U) + \left(\frac{\partial \ln p(E)}{\partial E}\right)_{E=U} (E-U) + \cancel{\frac{1}{2}\left(\frac{\partial^2 \ln p(E)}{\partial E^2}\right)_{E=U}(E-U)^2}$$

$$+ \frac{1}{2}\left(\frac{\partial^2 \ln p(E)}{\partial E^2}\right)_{E=U} (E-U)^2 + \cdots$$

$T(E) \equiv T_0$ $\qquad T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$

$$\ln[p(E)] = \ln\left(\frac{W(E)}{Q}\right) - \beta \varepsilon$$

$$p(E) = \frac{W(E)\, e^{-\beta E}}{Q}$$

Q is a sum over E levels

$$S(E) = k \ln W(E) \quad ; \quad \left(\frac{\partial S(E)}{\partial E}\right)_{V,N} = \frac{1}{T(E)}$$

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$$\frac{\partial \ln p(E)}{\partial E} = \frac{\partial \ln W(E)}{\partial E} - \beta = \frac{\partial (S/k)}{\partial E} - \beta$$

$$= \frac{1}{k} \cdot \frac{1}{T(E)} - \frac{1}{kT_o}$$

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v \quad ; \quad \frac{\partial^2 \ln p(E)}{\partial E^2} = \frac{1}{kT^2}\left(\frac{\partial T}{\partial E}\right)_{E=u} = \frac{1}{kT_o^2 C_v}$$

$$p(E) = p(u)\, e^{-(E-u)^2/2kT^2 C_v}$$

$$\boxed{p(E) = e^{[u - T_o S(u)]}\, e^{-(E-u)^2/2kT^2 C_v}}$$

This is a <u>Gaussian Function</u>.

Variance. $\sigma^2 = \langle (x-a)^2 \rangle$

$$\sigma^2 = \langle (E-u)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

$$= \langle E^2 \rangle - u^2 = kT_o^2 C_v$$

Standard Deviation: $\sigma = \sqrt{\sigma^2} = \sqrt{kT_o^2 C_v} \qquad \sigma \sim \sqrt{C_v}$

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The width of the energy fluctuations is proportional to C_v.

C_v is extensive; $C_v \sim N$.

$$\frac{\sigma_E}{E} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}$$

As $N \rightarrow 10^{23}$, $\frac{1}{\sqrt{N}} \rightarrow 0$.
Thus, fluctuation become very small for molar amounts.

Do. Example 12.2