Course 565/665 Lecture Number ____ Date 3/31/03

Lecturer Dr. Silvia Cavagnero Note Taker Eric Fulmer

Scholky Model for 2 State Systems

$E_2 = \varepsilon_0$

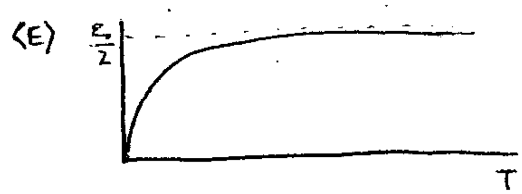
$E_1 = 0$

$$q = \sum_{i=1}^{2} e^{-\beta E_i} = e^{-\beta(0)} + e^{-\beta\varepsilon_0}$$

$$\boxed{q = 1 + e^{-\beta\varepsilon_0}}$$

$$\langle E \rangle = \frac{\sum_{i=1}^{2} E_i e^{-\beta E_i}}{\sum_{i=1}^{2} e^{-\beta E_i}} = \frac{0 + \varepsilon_0 e^{-\beta\varepsilon_0}}{1 + e^{-\beta\varepsilon_0}}$$

$$\boxed{\langle E \rangle = \frac{\varepsilon_0 e^{-\beta\varepsilon_0}}{1 + e^{-\beta\varepsilon_0}}}$$



In the low T limit $(T \to 0)$, $1/T \to \infty$, $e^{-1/T} \to 0$

$$\langle E \rangle = \frac{\varepsilon_0 (0)}{1 + 0} = 0$$

All molecules are in the ground state.

In the high T limit $(T \to \infty)$ we must expand the exponentials with Taylor Series expansions.

$$\langle E \rangle = \frac{\varepsilon_0 \left(1 + \frac{-E}{kT}\right)}{1 + \left(1 + \frac{-E}{kT}\right)} \simeq \frac{\varepsilon_0 (1 + 0)}{1 + (1 - 0)} = \frac{\varepsilon_0}{2}$$

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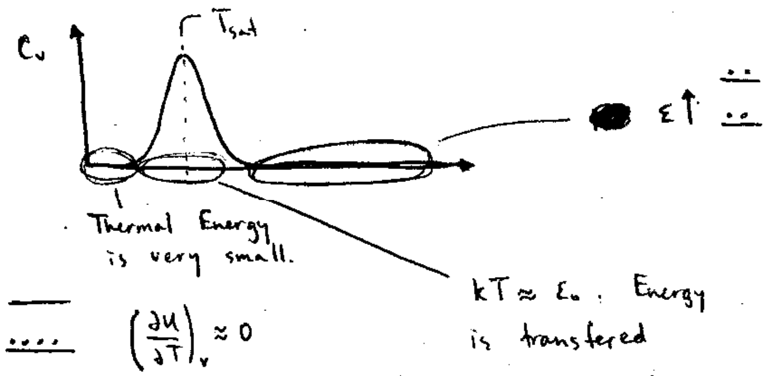
Thus, the energy levels are equalized in terms of populations.

<u>Heat Capacity</u>:

$$C_\alpha = \left(\frac{\partial q}{\partial T}\right)_\alpha \quad ; \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_v = \frac{N\varepsilon_0^2}{kT^2\left(1+e^{-\beta\varepsilon_0}\right)}$$



$$\frac{S}{N} = k \ln\left(1 - e^{-\beta\varepsilon_0}\right) + \frac{\varepsilon_0\, e^{-\beta\varepsilon_0}}{T\left(1 - e^{-\beta\varepsilon_0}\right)}$$

$$\frac{F}{NkT} = -\ln\left(1 + e^{-\beta\varepsilon_0}\right) = -\ln q$$

$$F = -kTN \ln q = -kT \ln q^N = -kT \ln Q$$

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Ensemble – A collection of all of the possible microstates of a system (a macroscopic system).

Some Ensembles

- Cannonical → T, V, N constant.
- Isobaric - Isothermal → T, p, N constant
- Grand Cannonical → T, ▮, V, μ constant.
- Microcannonical → E, V, N (or U, V, N)

Note also that each ensemble has a respective thermodynamic quantity associated with it. Just as the cannonical ensemble was directly related to Helmholtz free energy [$F = F(T, V, N)$].

Cannonical	Helmholtz
Isobaric - Isothermal	Gibbs
Microcannonical	T. Entropy
Grand Cannonical	(pV) ← [we haven't talked about this one.]

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- We can think about the first 3 ensembles (those dependent upon T) as immersed in a heat bath. This allows for U fluctuations.

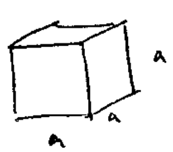
- The microcannonical ensemble has no bath, no U exchange at boundaries, and thus no U fluctuations.

Skip Chapter 11 (Read if you want to learn more about Quantum Mechanics).

Chapter 12

- Skip 1st part: "T".

Energy Fluctuations and Heat Capacity



- System constrained in a 3D box
- Use some particle in a box results.

From QM: $\varepsilon = \varepsilon_{n_x, n_y, n_z} = \dfrac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$

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The n's are quantum number, describing the energy level occupied by a given particle.

Space of Integers

$\boxed{2D}$ $R = (n_x^2 + n_y^2)^{1/2}$ in 2D case

Extend to 3D case: $V = \frac{4}{3}\pi R^3$

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

\# possible integers in a 3D space.