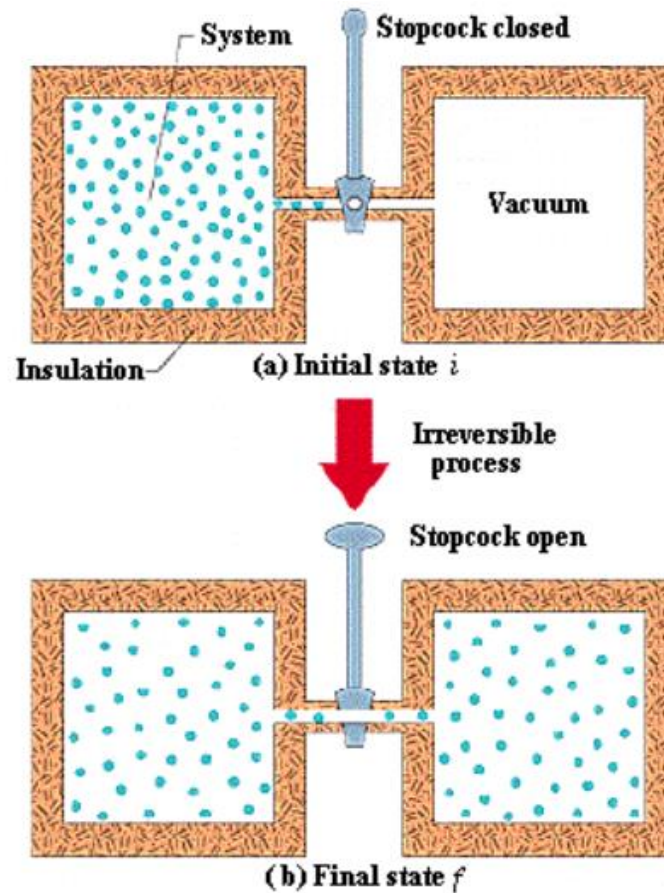


# Thermodynamics and Statistical Mechanics

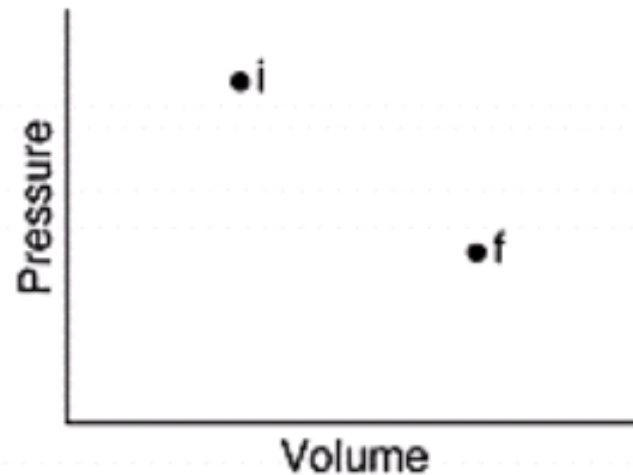
## Partition Function

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# Free Expansion of a Gas

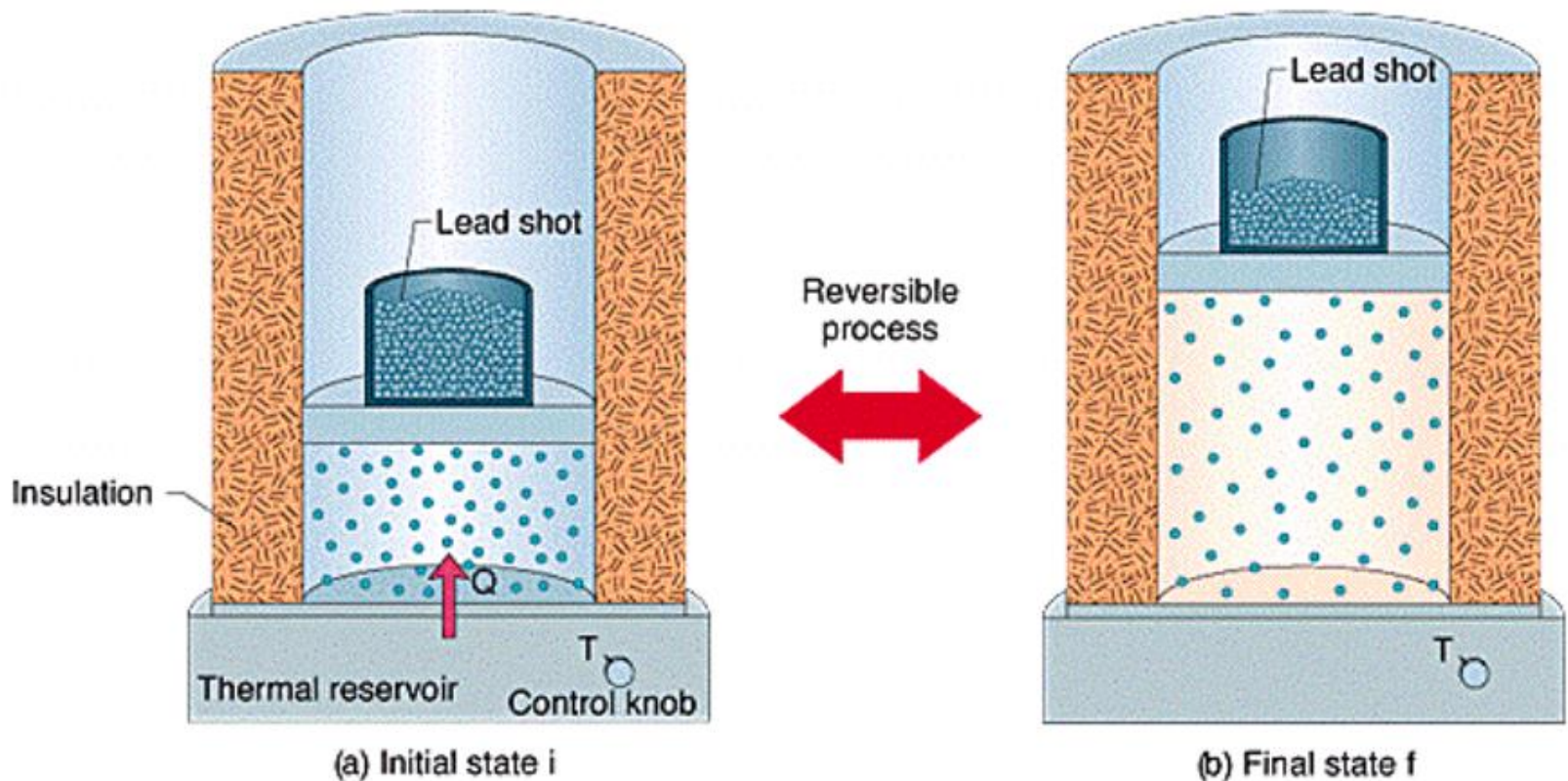


# Free Expansion



A  $p$ - $V$  diagram showing the initial state  $i$  and the final state  $f$  of the free expansion

# Isothermal Expansion



# Isothermal Expansion

Reversible route between same states.

$$\Delta S = \int_i^f \frac{dQ}{T} \quad \begin{array}{l} dQ = dW + dU \\ \text{Since } T \text{ is constant, } dU = 0. \\ \text{Then, } dQ = dW. \end{array}$$

$$dW = PdV = \frac{nRT}{V} dV$$

$$dS = \frac{dQ}{T} = \frac{dW}{T} = \frac{nRT}{T} \frac{dV}{V} = nR \frac{dV}{V}$$

# Entropy Change

$$\Delta S = nR \int_V^{2V} \frac{dV}{V} = nR \ln \left( \frac{2V}{V} \right) = nR \ln 2$$

The entropy of the gas increased.

For the isothermal expansion, the entropy of the Reservoir decreased by the same amount.

So for the system plus reservoir,  $\Delta S = 0$

For the free expansion, there was no reservoir.

# Statistical Approach

$$\Delta S = S_f - S_i = k \ln w_f - k \ln w_i = k \ln \left( \frac{w_f}{w_i} \right)$$

$$w_i = \frac{N!}{N!0!} = 1$$

$$w_f = \frac{N!}{(N/2)!(N/2)!} = \frac{N!}{[(N/2)!]^2}$$

# Statistical Approach

$$\Delta S = k \ln \left( \frac{w_f}{w_i} \right) = k \ln \left( \frac{N!}{[(N/2)!]^2} \right)$$

$$\Delta S = k[\ln N! - 2 \ln(N/2)!]$$

$$\Delta S = k[N \ln N - N - 2\{(N/2) \ln(N/2) - N/2\}]$$

$$\Delta S = k[N \ln N - N \ln(N/2)] = Nk \ln \left( \frac{N}{N/2} \right)$$

$$\Delta S = Nk \ln 2 = nR \ln 2$$



# Partition Function

$$N_j = N \frac{g_j e^{-\beta \epsilon_j}}{\sum_{j=1}^n g_j e^{-\beta \epsilon_j}}$$

$$\sum_{j=1}^n g_j e^{-\beta \epsilon_j} = Z \quad \text{Partition Function}$$

$$N_j = N \frac{g_j e^{-\beta \epsilon_j}}{Z}$$

# Boltzmann Distribution

$$N_j = N \frac{g_j e^{-\beta \varepsilon_j}}{\sum_{j=1}^n g_j e^{-\beta \varepsilon_j}}$$

$$\sum_{j=1}^n \varepsilon_j N_j = U = N \frac{\sum_{j=1}^n \varepsilon_j g_j e^{-\beta \varepsilon_j}}{\sum_{j=1}^n g_j e^{-\beta \varepsilon_j}}$$

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

# Maxwell-Boltzmann Distribution

Correct classical limit of quantum statistics is Maxwell-Boltzmann distribution, not Boltzmann.

What is the difference?

# Maxwell-Boltzmann Probability

$$w_{BE} = \prod_{j=1}^n \frac{(N_j + g_j - 1)!}{N_j! (g_j - 1)!}$$

$$w_{FD} = \prod_{j=1}^n \frac{g_j!}{N_j! (g_j - N_j)!}$$

$$w_B = N! \prod_{j=1}^n \frac{g_j^{N_j}}{N_j!}$$

$$w_{MB} = \prod_{j=1}^n \frac{g_j^{N_j}}{N_j!}$$

$w_B$  and  $w_{MB}$  yield the same distribution.

# Relation to Thermodynamics

$$U = \sum_j N_j \varepsilon_j$$

$$dU = \sum_j \varepsilon_j dN_j + \sum_j N_j d\varepsilon_j$$

$$\varepsilon_j = \varepsilon_j(X), \quad \text{so} \quad d\varepsilon_j = \frac{d\varepsilon_j}{dX} dX$$

$$dU = \sum_j \varepsilon_j dN_j + \sum_j \left[ N_j \frac{d\varepsilon_j}{dX} \right] dX$$

$$\text{Call} \quad \sum_j \left[ N_j \frac{d\varepsilon_j}{dX} \right] = -Y$$

# Relation to Thermodynamics

$$dU = \sum_j \varepsilon_j dN_j + \sum_j \left[ N_j \frac{d\varepsilon_j}{dX} \right] dX \quad \text{and} \quad \sum_j \left[ N_j \frac{d\varepsilon_j}{dX} \right] = -Y$$

$$dU = \sum_j \varepsilon_j dN_j - YdX \quad \text{This is like}$$

$$dU = TdS - YdX \quad (\text{or } dU = TdS - PdV)$$

If  $dX = 0$

$$(dU)_X = \sum_j \varepsilon_j dN_j = TdS \quad \text{and} \quad \sum_j N_j d\varepsilon_j = -YdX$$

# Chemical Potential

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

In this equation,  $\mu$  is the chemical energy per molecule, and  $dN$  is the change in the number of molecules.

# Chemical Potential

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

$$F = U - TS$$

$$dF = TdS - PdV + \mu dN - TdS - SdT$$

$$dF = -SdT - PdV + \mu dN$$

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



# Entropy

$$S = k \ln w_{MB} \quad \text{where} \quad w_{MB} = \prod_{j=1}^n \frac{g_j^{N_j}}{N_j!}$$

$$S = k \left[ \sum_j N_j \ln g_j - \sum_j \ln N_j! \right]$$

$$S = k \left[ \sum_j N_j \ln g_j - \sum_j N_j \ln N_j + \sum_j N_j \right]$$

$$S = k \left[ N - \sum_j N_j \ln \left( \frac{N_j}{g_j} \right) \right]$$

# Entropy

$$S = k \left[ N - \sum_j N_j \ln \left( \frac{N_j}{g_j} \right) \right]$$

$$\frac{N_j}{g_j} = \frac{N}{Z} e^{-\frac{\epsilon_j}{kT}}$$

$$S = k \left[ N - \sum_j N_j \ln N + \sum_j N_j \ln Z + \sum_j N_j \frac{\epsilon_j}{kT} \right]$$

$$S = \frac{U}{T} + Nk(\ln Z - \ln N + 1)$$

# Helmholtz Function

$$S = \frac{U}{T} + Nk(\ln Z - \ln N + 1)$$

$$F = U - TS = U - T \frac{U}{T} - NkT(\ln Z - \ln N + 1)$$

$$F = -NkT(\ln Z - \ln N + 1)$$

# Chemical Potential

$$F = -NkT(\ln Z - \ln N + 1)$$

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

$$\mu = -kT(\ln Z - \ln N + 1) - NkT \left( -\frac{1}{N} \right)$$

$$\mu = kT(\ln N - \ln Z) = kT \ln \left( \frac{N}{Z} \right)$$

# Chemical Potential

$$\mu = kT \ln\left(\frac{N}{Z}\right) \quad \text{so} \quad \frac{\mu}{kT} = \ln\left(\frac{N}{Z}\right)$$

$$\text{Then} \quad e^{\frac{\mu}{kT}} = \frac{N}{Z}$$

$$\text{So,} \quad \frac{\mu}{kT} = -\alpha$$

# Boltzmann Distribution

$$N_j = e^{-\alpha} g_j e^{-\beta \epsilon_j}$$

$$\sum_{j=1}^n N_j = N = e^{-\alpha} \sum_{j=1}^n g_j e^{-\beta \epsilon_j}$$

$$e^{-\alpha} = \frac{N}{\sum_{j=1}^n g_j e^{-\beta \epsilon_j}}$$

$$N_j = N \frac{g_j e^{-\beta \epsilon_j}}{\sum_{j=1}^n g_j e^{-\beta \epsilon_j}}$$

# Distributions

$$\frac{N_j}{g_j} = \frac{1}{e^{\alpha + \beta \varepsilon_j}} = f_j$$

Boltzmann

$$\frac{N_j}{g_j} = \frac{1}{e^{\alpha + \beta \varepsilon_j} - 1} = f_j$$

Bose - Einstein

$$\frac{N_j}{g_j} = \frac{1}{e^{\alpha + \beta \varepsilon_j} + 1} = f_j$$

Fermi - Dirac

# Distributions

$$\frac{N_j}{g_j} = \frac{1}{e^{\frac{\varepsilon_j - \mu}{kT}}} = f_j$$

Boltzmann

$$\frac{N_j}{g_j} = \frac{1}{e^{\frac{\varepsilon_j - \mu}{kT}} - 1} = f_j$$

Bose - Einstein

$$\frac{N_j}{g_j} = \frac{1}{e^{\frac{\varepsilon_j - \mu}{kT}} + 1} = f_j$$

Fermi - Dirac



# Ideal Gas

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

$$F = -NkT(\ln Z - \ln N + 1)$$

$$F = -NkT \left[ \ln V + \frac{3}{2} \ln \left( \frac{2\pi mkT}{h^2} \right) - \ln N + 1 \right]$$

# Ideal Gas

$$F = -NkT \left[ \ln V + \frac{3}{2} \ln \left( \frac{2\pi mkT}{h^2} \right) - \ln N + 1 \right]$$

$$P = - \left( \frac{\partial F}{\partial V} \right)_{T,N} = NkT \frac{1}{V}$$

$$PV = NkT = nRT$$

# Ideal Gas

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

$$\ln Z = \ln V \left( \frac{2\pi m}{h^2} \right)^{3/2} - \frac{3}{2} \ln \beta$$

$$\frac{U}{N} = - \frac{\partial \ln Z}{\partial \beta} = \frac{3}{2} \frac{1}{\beta} = \frac{3}{2} kT$$

# Entropy

$$S = \frac{U}{T} + Nk(\ln Z - \ln N + 1)$$

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

$$S = \frac{3NkT}{2T} + Nk \left( \ln \frac{V}{N} \left( \frac{2\pi mkT}{h^2} \right)^{3/2} + 1 \right)$$

$$S = Nk \left( \frac{5}{2} + \ln \frac{V}{N} \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \right)$$

# Math Tricks

For a system with levels that have a constant spacing (e.g. harmonic oscillator) the partition function can be evaluated easily. In that case,  $\varepsilon_n = n\varepsilon$ , so,

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} e^{-\beta \varepsilon_n} = \sum_{n=0}^{\infty} e^{-\beta n \varepsilon} = \sum_{n=0}^{\infty} \left( e^{-\beta \varepsilon} \right)^n \\ &= \sum_{n=0}^{\infty} x^n = \frac{1}{1-x} = \frac{1}{1-e^{-\beta \varepsilon}} \quad \text{for } e^{-\beta \varepsilon} < 1. \end{aligned}$$

# Heat Capacity of Solids

Each atom has 6 degrees of freedom, so based on equipartition, each atom should have an average energy of  $3kT$ . The energy per mole would be  $3RT$ . The heat capacity at constant volume would be the derivative of this with respect to  $T$ , or  $3R$ . That works at high enough temperatures, but approaches zero at low temperature.

# Heat Capacity

Einstein found a solution by treating the solid as a collection of harmonic oscillators all of the same frequency. The number of oscillators was equal to three times the number of atoms, and the frequency was chosen to fit experimental data for each solid. Your class assignment is to treat the problem as Einstein did.

# Heat Capacity

