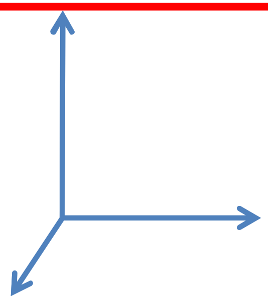
# Thermodynamics in 15 Minutes

Charles E. Sing
DMSE/PPST

*Bird's Eye View of ENERGY*

$$dU = \sum_i F_i dx_i = \sum_i \left(\frac{\partial U}{\partial x_i}\right)_{x_{j \neq i}} dx_i$$

**There is a potential ENERGY (U) that represents the sum of system descriptors (Coordinates) times their respective partials with respect to energy (Forces).**



$$-\mathbf{P}, \gamma, \mathcal{H}, \mathcal{E}$$

$$\mathbf{V}, \mathbf{A}, \mathcal{M}, \mathcal{P}$$

$$\hat{x}_i \cdot \hat{x}_j = \delta_{ij}$$

**Generally, all coordinate axis are orthogonal…**

**How do we fit heat into this equation?**

**S? T?**

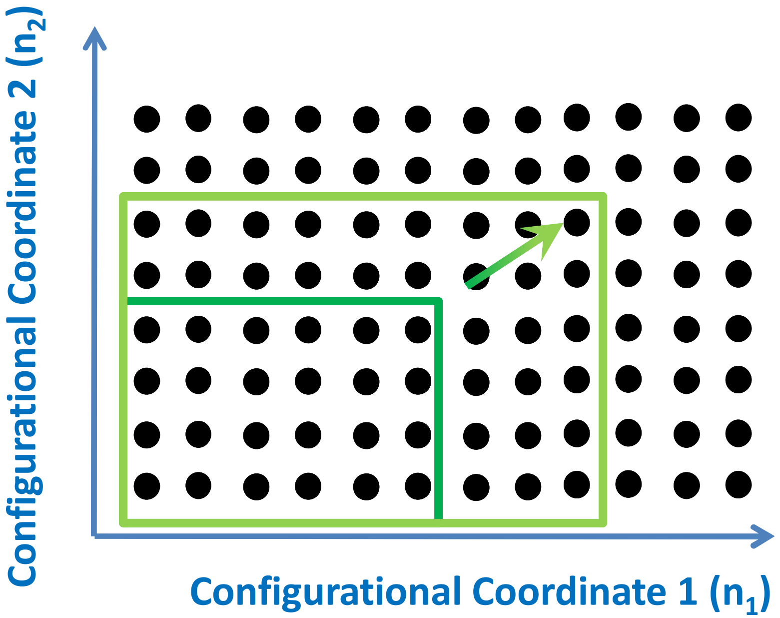
# Introducing HEAT

*Meet the new boss, same as the old boss…only in PHASE SPACE!*

$$\delta W = -PdV = \sum_i F_i dx_i$$

$$\delta Q = \sum_i F_{i,conf} dx_{i,conf}$$

**Analogy between P-V and T-S**




$$F_{i,conf} \rightarrow \sim kT/n_i$$

$$dx_{i,conf} \rightarrow dn_i$$

$$\delta Q_i = \frac{kT}{n_i} dn_i = Td(k \ln n_i) =$$
$$= TdS_i$$

*Here we invoke equipartition – a bit circular, so NOT a rigorous proof!

**Complete Equation:**

$$\mathbf{dU} = \delta\mathbf{Q} + \delta\mathbf{W} = \left(\frac{\partial \mathbf{U}}{\partial \mathbf{S}}\right)_{\mathbf{V},\mathbf{N},\cdots} \mathbf{dS} + \left(\frac{\partial \mathbf{U}}{\partial \mathbf{V}}\right)_{\mathbf{S},\mathbf{N},\cdots} \mathbf{dV} + \left(\frac{\partial \mathbf{U}}{\partial \mathbf{N}}\right)_{\mathbf{V},\mathbf{S},\cdots} \mathbf{dN} + \cdots$$

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$\mathbf{T}$ $\quad -\mathbf{P}$ $\quad \mu$

**Needs Inputs:**

$$\left(\frac{\partial \mathbf{U}}{\partial \mathbf{S}}\right)_{\mathbf{V},\mathbf{N},\cdots} = \mathbf{T}(\mathbf{S},\mathbf{V},\mathbf{N},\cdots)$$

**Equations of State: First Partial Derivatives**
**(But how do we determine these?)**

# Back to the FUNdamental equation

## *The Hierarchy*

**Complete Equation:**

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**Equations of State: First Partial Derivatives**
**(But how do we determine these?)**

**Which Need Parameters:**

$$\left(\frac{\partial^2 \mathbf{U}}{\partial \mathbf{S} \partial \mathbf{V}}\right)_{\mathbf{P},\mathbf{N},\cdots} - \frac{1}{\mathbf{V}\alpha}$$

**Material Constants: Second Partial Derivatives**
**(Determined Experimentally or w/ Stat Mech)**

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## *The Hierarchy*

**Complete Equation:**

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**Relationships at each level lowers degrees of freedom:**

$$\mathbf{SdT} - \mathbf{VdP} + \mathbf{N}\mathbf{d}\mu = \mathbf{0}$$

$$\left(\frac{\partial}{\partial \mathbf{S}}\left(\frac{\partial \mathbf{U}}{\partial \mathbf{V}}\right)_{\mathbf{S,N}}\right)_{\mathbf{V,N}} = \left(\frac{\partial}{\partial \mathbf{V}}\left(\frac{\partial \mathbf{U}}{\partial \mathbf{S}}\right)_{\mathbf{V,N}}\right)_{\mathbf{S,N}}$$

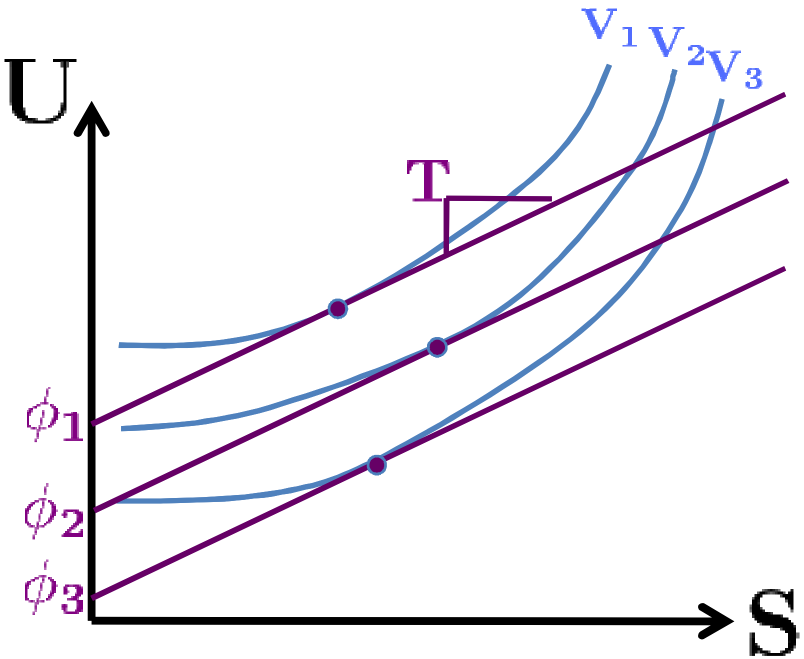
*Addition of Constraints*

**How do we take this:**

$$U(S, V, N) = TS - PV + \mu N$$

**And incorporate this:**

$$T = \text{Constant}$$




**Or this:**

$$P = \text{Constant}$$

**Define a new potential:**

$$\phi_i = U_i - TS_i$$

**This is Helmholtz Free Energy! We can define others depending on specific constraints.**

**Previously we determined:**

$$\mathbf{S = k \ln n \rightarrow S_i = -Nk(P_i \ln P_i)}$$

**And we just derived for a constant T system:**

$$\mathbf{F_i = U_i - TS_i}$$

**Combine these to get:**

$$\mathbf{N_i(F_i - U_i) = kTN_i \ln P_i}$$

$$\mathbf{P_i = e^{-U_i/kT} e^{F/kT} = \frac{e^{-U_i/kT}}{Q}}$$

**Since $P_i$ must be normalized:**

$$\mathbf{Q = \sum_i e^{-U_i/kT} = \sum_U n(U) e^{-U/kT}}$$

*The Microscopic Picture*

$$Q = \sum_i e^{-U_i/kT} = \sum_U n(U) e^{-U/kT}$$

Replace summation by most likely value (*) (large N)

$$Q \approx e^{\ln n^* - U^*/kT} = e^{-F^*/kT}$$

$$F^* = -kT \ln Q$$

Plug this BACK INTO THERMO EQUATIONS!

$$dF = -TdS - PdV$$

$$-kT \left( \frac{\partial \ln Q}{\partial V} \right)_S = -P$$

# Conclusion

*Map of Thermo*

FUNDAMENTAL EQUATION

$$\mathbf{dU = \sum_i F_i dx_i}$$

Constraints j

$$\phi = \mathbf{U} - \sum_j \mathbf{F_j x_j}$$

Legendre Transforms

$$\left(\frac{\partial \mathbf{U}}{\partial \mathbf{x_i}}\right)_{\mathbf{x_{j \neq i}}}$$

EOS

$$\mathbf{S = k \ln n}$$

Macro vs. Micro

$$\left(\frac{\partial^2 \mathbf{U}}{\partial \mathbf{x_i} \partial \mathbf{x_j}}\right)_{\mathbf{x_{k \neq i,j}}}$$

Material Parameters

$$\mathbf{Q} = \sum_i \mathbf{e}^{-\frac{(\phi_i + \mathbf{TS_i})}{\mathbf{kT}}}$$

Partition Functions