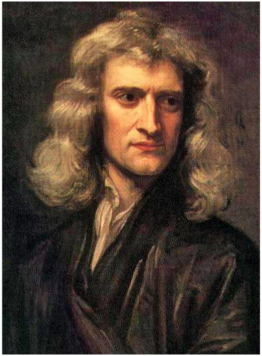
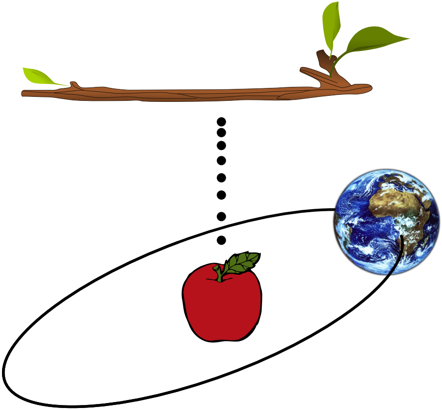
Everything you Need to Know about Classical Thermodynamics

MSE 421 - Ceriotti

From classical mechanics to statistical mechanics





Isaac Newton (1643-1727): kinematic theory of macroscopic bodies

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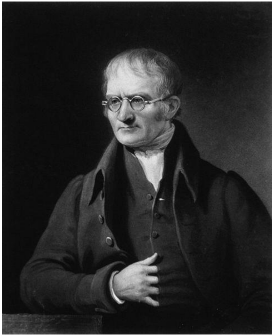

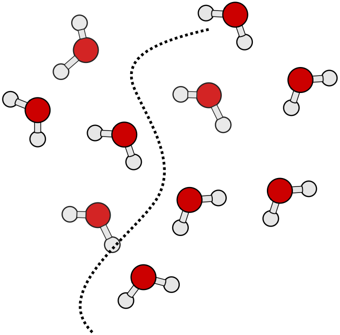

John Dalton (1766 - 1844): atomic theory and kinetic theory of gases

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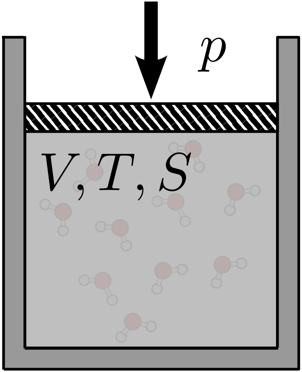

Sadi Carnot (1796-1832): phenomenological thermodynamics. Theory of heat, work, engines

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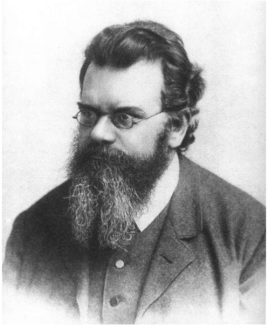
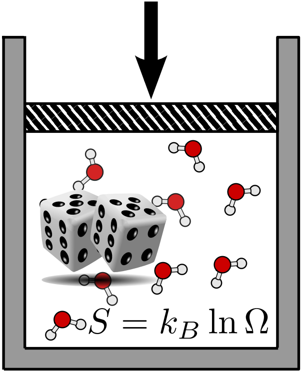
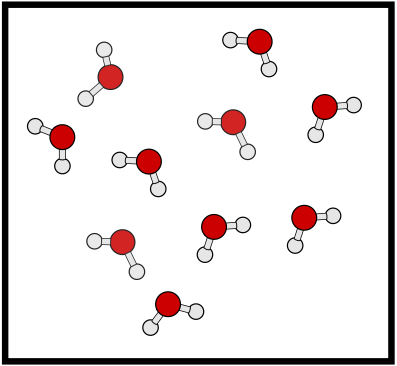




Ludwig Boltzmann (1844-1906): statistical mechanics: reconcile molecular picture and macroscopic thermodynamics

Microstates and Macrostates

- The task of measuring position and velocities of a macroscopic amount of atoms or molecules is practically impossible
- We can characterize the macroscopic state of *equilibrium* systems by a small number of macroscopic observables, e.g. volume V, temperature T, pressure p, molar amounts of components n_i



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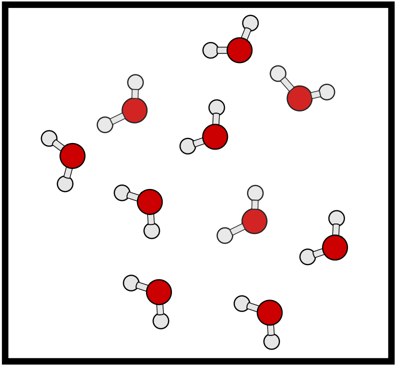

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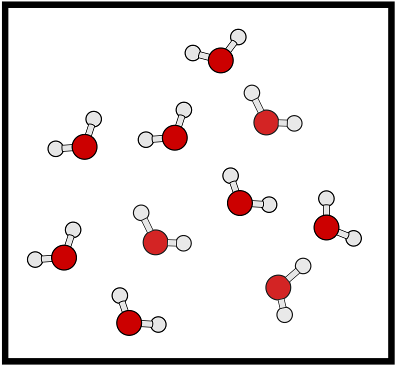

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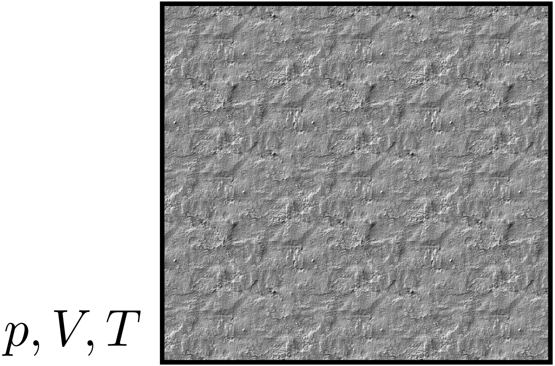
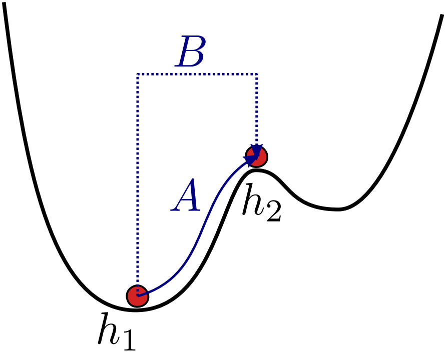


Thermodynamic variables

- *State variables* are macroscopic quantities that only depend on the state of the system and not on how the system has been prepared (e.g. T, p, E, V, n, . . .)
  - Infinitesimal changes in state variables are exact differentials (e.g. $\int_{V_1}^{V_2} \mathrm{d}V = V_2 - V_1$, irrespective of the path)
  - *Extensive* variables (n, V) double when system size is doubled. *Intensive* variables (e.g. T, p) do not depend on system size



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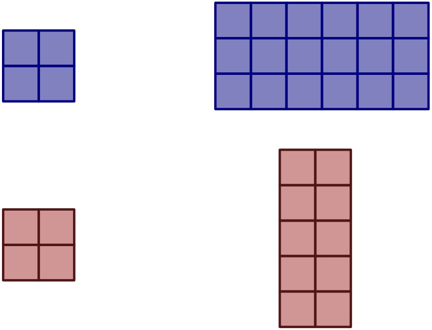
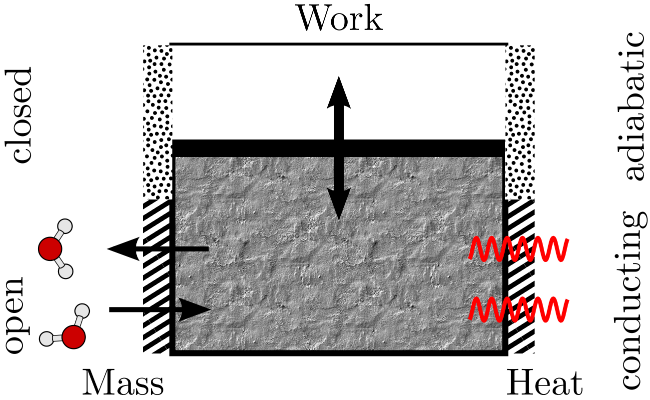


Boundary Conditions

- The boundary of the system can be open or closed relative to the exchange of mass, and conducting or adiabatic relative to exchange of heat with its surroundings (closed+adiabatic≡isolated)
- The state of the system can also be changed by application of work

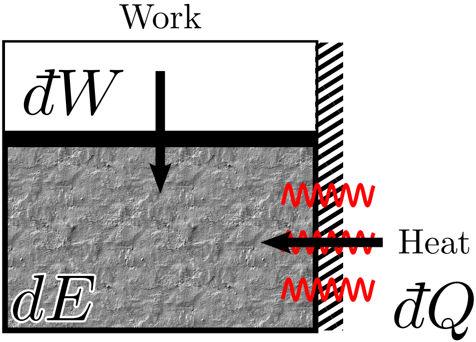


The internal energy *E*

- The internal energy is a function of state that expresses the potential the system has to generate work. Can be defined by assuming it is
  1. Extensive ($E = E_1 + E_2$)
  2. Conserved. Can change by doing **work**, or by exchanging **heat**

$$\boxed{\mathrm{d}E = đW + đQ}$$ **First Law**

  3. Note the (arbitrary) convention for the sign of differentials.



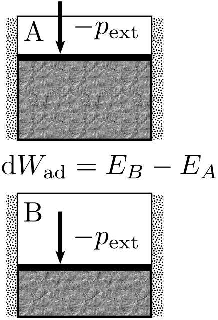
The internal energy is also indicated as U in many books. d indicates an exact differential, đ indicates an inexact differential, and depends on the path followed during a transformation.

Measuring the change in internal energy

- Work is associated with change of one of the extensive mechanical variables X defining the state of the system
- For each variable there is a (generalized) force f that links it with the work done by changing it (e.g. $đW = -p_{\mathrm{ext}}\mathrm{d}V$)

$$đW = f\mathrm{d}X,$$

- We can *measure* $\mathrm{d}E$ as the work spent doing an *adiabatic* transformation between two states A and B

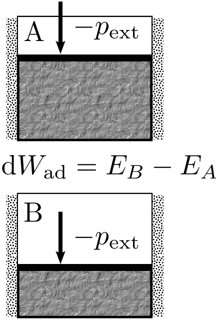


$$\mathrm{d}W_{\mathrm{ad}} = E_B - E_A$$

The first law as the definition of heat

- We can consider the first law as the *definition* of heat
  1. Do an adiabatic transformation to measure the change in internal energy $E_B - E_A$
  2. Repeat with open walls, measure the new work $\text{đ}W$ and obtain $\text{đ}Q$ as the difference

$$\text{đ}Q = \mathrm{d}W_{\mathrm{ad}} - \text{đ}W$$



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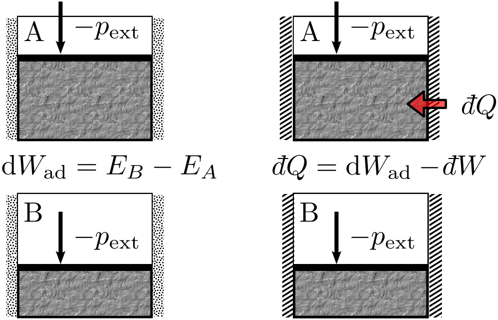
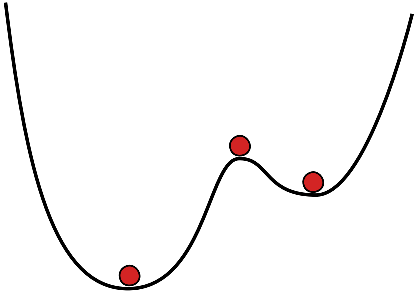


Equilibrium and transformations

- *Equilibrium* states do not change unless perturbed. If the system returns to a state after a small perturbation, it is said to be *stable*.
- An *equation of state* $f(\mathbf{X}) = f(E, V, n_i, \ldots) = 0$, determines which values of thermodynamic variables are compatible with equilibrium
- *Reversible* transformations proceed along a series of equilibrium states. *Irreversible* transformations traverse values of thermodynamic variables that violate the EoS.



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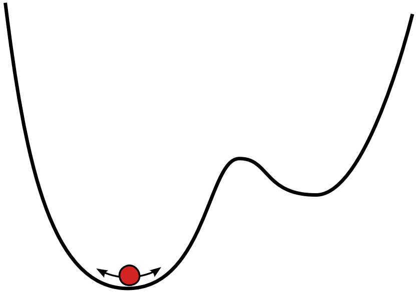

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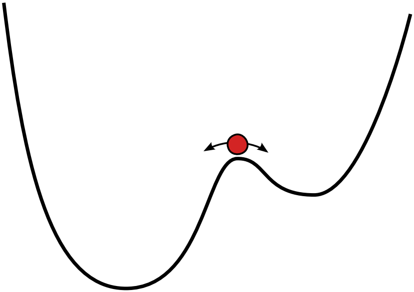

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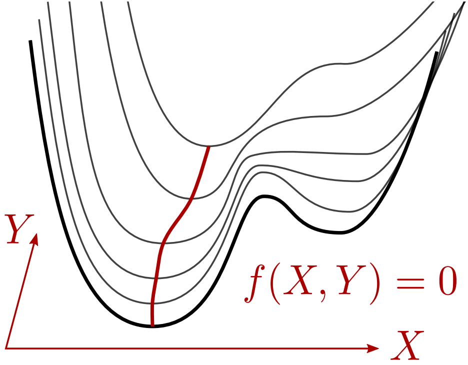

E.g. for a perfect gas, $pV - nRT = 0$

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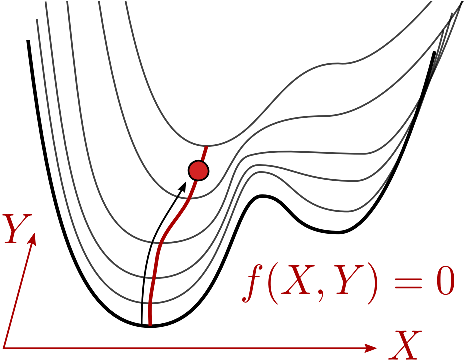

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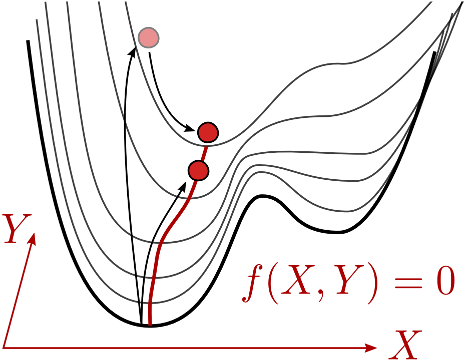
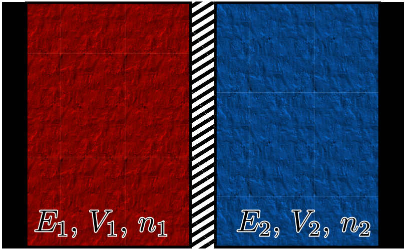


The search for equilibrium states

- How do we determine if a system is in equilibrium?
- How do we determine *what* is the equilibrium state of a system?
- How do we determine the evolution of a system after we remove some *internal constraints*?
- We can try to define a single state function to answer all these questions: entropy!



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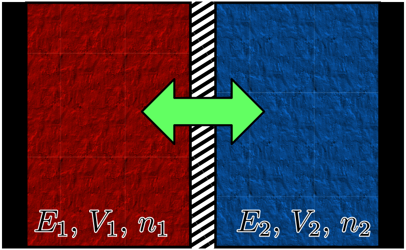

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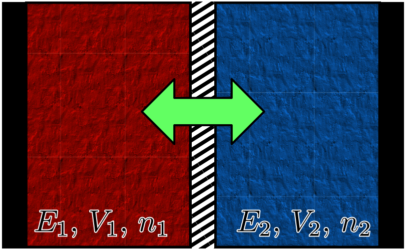
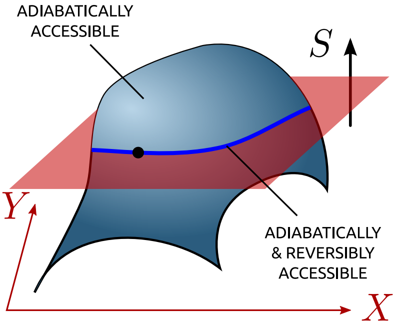


An axiomatic definition of entropy

- *Define* the entropy $S\left(E,\mathbf{X}\right)$ as
  1. Extensive function of state
  2. Monotonically-increasing function of E
     - *Define* the temperature as $\left(\partial E/\partial S\right)_{\mathbf{X}}=\left[\left(\partial S/\partial E\right)_{\mathbf{X}}\right]^{-1}=T>0$
  3. If it is possible to obtain state B *adiabatically* from state A, then $S\left(B\right)\geq S\left(A\right)$

     $\boxed{\Delta S_{\text{ad}}\geq 0}$ Second Law

  4. If a process is reversible, then one can also reach *adiabatically* A from B, that implies $S\left(B\right)=S\left(A\right)$



Entropy and reversible heat

- Consider a system defined by S, E, and mechanical variables $\mathbf{X}$. For a reversible process one can cast the EOS into $S = S(E, \mathbf{X})$
- Compare the differentials of S and E

$$\overbrace{\mathrm{d}S = \left(\frac{\partial S}{\partial E}\right)_{\mathbf{X}} \mathrm{d}E + \sum_i \left(\frac{\partial S}{\partial X_i}\right)_{E,\mathbf{X}'_i} \mathrm{d}X_i}^{\text{total differential of } S(E,\mathbf{X})} \qquad \overbrace{\mathrm{d}E = \text{đ}Q_{\mathrm{rev}} + \text{đ}W_{\mathrm{rev}}}^{\text{first law}}$$

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- For an adiabatic, reversible process $\mathrm{d}S = 0$ and $\text{đ}Q = 0$

$$0 = \sum_i \frac{1}{T}\frac{\partial E}{\partial X_i}\mathrm{d}X_i + \sum_i \left(\frac{\partial S}{\partial X_i}\right)_{E,\mathbf{X}'_i} \mathrm{d}X_i \Rightarrow \left(\frac{\partial E}{\partial X_i}\right)_{S,\mathbf{X}'_i} = -T\left(\frac{\partial S}{\partial X_i}\right)_{E,\mathbf{X}'_i}$$

- Considering a reversible but non-adiabatic process

$$\underbrace{\boxed{T\mathrm{d}S = \text{đ}Q_{\mathrm{rev}}}}_{\text{Clausius principle}}, \qquad \mathrm{d}E = T\mathrm{d}S + \sum_i \left(\frac{\partial E}{\partial X_i}\right) \mathrm{d}X_i$$

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Here we *postulate* it, and derive Clausius's principle from the postulated properties of S.

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$$0 = \sum_i \frac{1}{T} \frac{\partial E}{\partial X_i} \mathrm{d}X_i + \sum_i \left(\frac{\partial S}{\partial X_i}\right)_{E,\mathbf{X}'_i} \mathrm{d}X_i \Rightarrow \left(\frac{\partial E}{\partial X_i}\right)_{S,\mathbf{X}'_i} = -T \left(\frac{\partial S}{\partial X_i}\right)_{E,\mathbf{X}'_i}$$

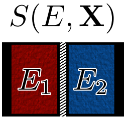
- Considering a reversible but non-adiabatic process

$$\underbrace{\boxed{T\mathrm{d}S = đQ_{\text{rev}}}}_{\text{Clausius principle}}, \qquad \mathrm{d}E = T\mathrm{d}S + \sum_i \left(\frac{\partial E}{\partial X_i}\right) \mathrm{d}X_i$$

Many classical books define the entropy starting from the reversible heat.
Here we *postulate* it, and derive Clausius's principle from the postulated properties of S.

Internal constraints and equilibrium

- Consider a system to which we applied an internal constraint - e.g. we fix the partitioning of E between two subsystems
  1. We start in equilibrium, and make an arbitrary transformation that only changes the partitioning of energy between the two subsystems. This gives a state with a different entropy S' but same energy $E = E_1 + E_2$: from the first law, $đQ + đW = 0$
  2. We relax back to equilibrium adiabatically. From the axioms: $S' < S$
- The equilibrium partitioning is the one that maximizes the entropy: $\Delta S_{\mathrm{adj}} \geq 0$ results in a general **maximum-entropy principle**



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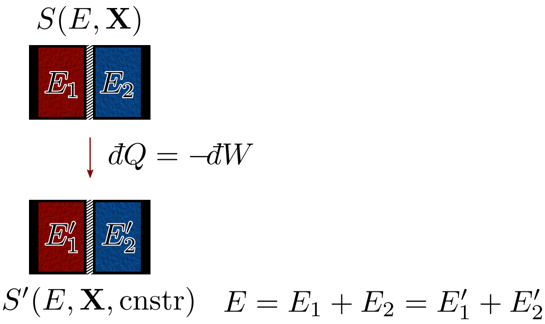

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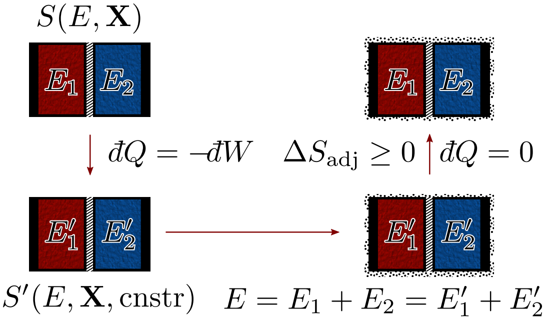

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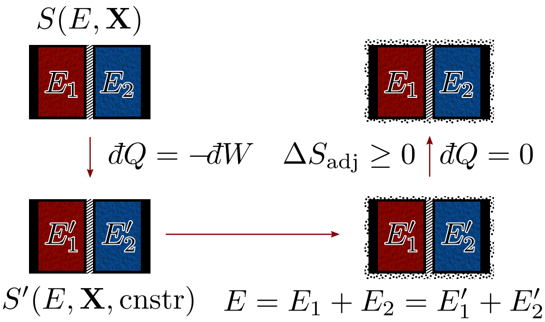
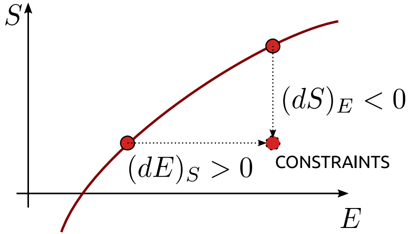


A variational principle for E

- Under the conservation conditions $E = E_1 + E_2$, $\mathbf{X} = \mathbf{X}_1 + \mathbf{X}_2$, and given the maximum entropy principle
$$S(E, \mathbf{X}, \text{cnstr}) = S(E_1, \mathbf{X}_1) + S(E_2, \mathbf{X}_2) \leq S(E, \mathbf{X})$$
Recall that $\partial S / \partial E > 0$. Then, if
$$S(E', \mathbf{X}) = S(E, \mathbf{X}, \text{cnstr})$$
it must be that $E' < E$. That is, introducing constraints at constant entropy necessarily implies an increase of internal energy.
- If we introduce infinitesimal constraints δY around equilibrium, we can express this condition as
$$\delta E_{S,\mathbf{X}} = E(S, \mathbf{X}, \delta Y) - E(S, \mathbf{X}) \approx \left(\frac{\partial E}{\partial Y}\right)_{S,\mathbf{X},\delta Y=0} \delta Y \geq 0$$



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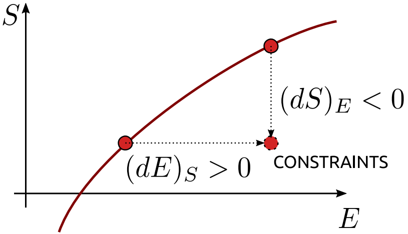

Thermal equilibrium

- What happens if we tried to partition energy between the two subsystems, at constant total energy?

$$\overbrace{0 \geq \delta S_{E,\mathbf{X}}}^{\text{maxent principle}} = \overbrace{\delta S_1 + \delta S_2}^{\text{extensive entropy}} = \left(\frac{\partial S_1}{\partial E_1}\right)_{\mathbf{X},\delta E_1=0} \delta E_1 + \left(\frac{\partial S}{\partial E_2}\right)_{\mathbf{X},\delta E_2=0} \delta E_2$$

- Due to the constant-energy condition, $\delta E_2 = -\delta E_1$, and considering that $\partial S/\partial E = 1/T$

$$\frac{1}{T_1}\delta E_1 + \frac{1}{T_2}\delta E_2 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\delta E_1 \leq 0 \quad \text{for all } \delta E_1\text{, that implies} \quad T_1 = T_2$$

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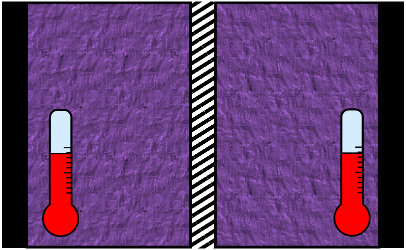

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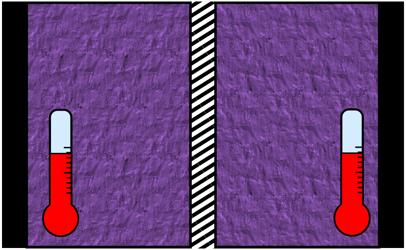


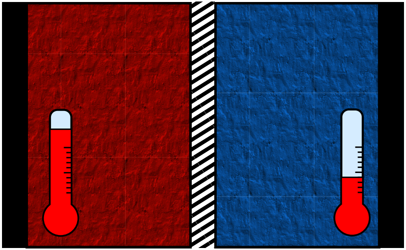
Convergence to thermal equilibrium

- Now consider an initial state $T_1 \neq T_2$. An adiabatic spontaneous evolution will have $\Delta S_1 + \Delta S_2 = \Delta S > 0$.

$$\left(\frac{\partial S_1}{\partial E_1}\right)_{\mathbf{X}} \Delta E_1 + \left(\frac{\partial S}{\partial E_2}\right)_{\mathbf{X}} \Delta E_2 > 0 \qquad \rightarrow \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Delta E_1 > 0$$

- The maximum entropy condition implies that energy flows from the hot to the cold subsystem

$$\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Delta E_1 > 0 \qquad T_2 > T_1 \rightarrow \frac{1}{T_2} < \frac{1}{T_1} \rightarrow \Delta E_1 > 0$$



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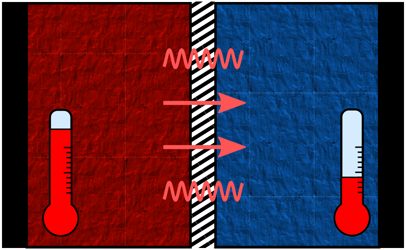


Legendre transforms

- Consider a function of N variables $f\left(x_1, \ldots, x_N\right)$. One can write its differential
$$\mathrm{d}f = \sum_i \frac{\partial f}{\partial x_i} \mathrm{d}x_i.$$
- Say we wanted to define a function, related to f, that instead has a differential form that depends on another set of variables u_i.
  - Consider $g = f - \sum_i x_i u_i$
$$\mathrm{d}g = \sum_i \frac{\partial f}{\partial x_i} \mathrm{d}x_i - \sum_i u_i \mathrm{d}x_i - \sum_i x_i \mathrm{d}u_i$$
  - If we set $u_i = \frac{\partial f}{\partial x_i}$ we can cancel the differentials $\mathrm{d}x_i$. This is the Legendre transform of f
$$\boxed{g\left(u_1, \ldots\right) = f - \sum_i x_i \frac{\partial f}{\partial x_i}}$$
- Obviously, the transform can be applied to a subset of the x_i's

Thermodynamic potentials

- The most important term of $\mathrm{d}E$ in terms of mechanical boundary conditions is $-p\mathrm{d}V$, that can be supplemented by composition variables. E is a natural function of S, V, n_i, so -- introducing the chemical potential $\mu_i = (\partial E/\partial n_i)_{S,V,\mathbf{n}_i'}$

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V + \sum_i \mu_i \mathrm{d}n_i.$$

  - One can Legendre-transform the entropy term, obtaining the Helmoltz free energy

$$A = E - TS, \qquad \mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V + \sum_i \mu_i \mathrm{d}n_i$$

. . . or the volume term obtaining the enthalpy

$$H = E + pV, \qquad \mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p + \sum_i \mu_i \mathrm{d}n_i$$

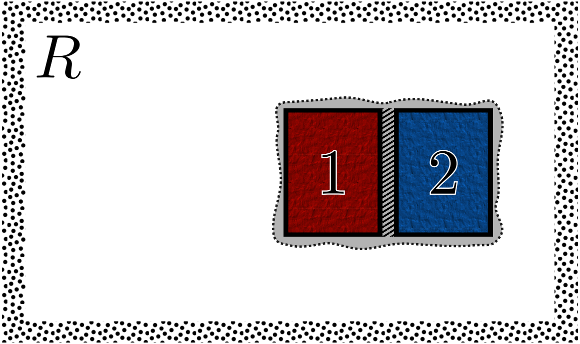
. . . or both obtaining the Gibbs free energy

$$G = E - TS + pV, \qquad \mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \sum_i \mu_i \mathrm{d}n_i$$

A variational principle for G

- Consider a composite system $1+2$ enclosed in a temperature/pressure reservoir R, at T^R and p^R

adiabaticity+constant-V $\rightarrow \mathrm{d}\left(E^1+E^2+E^R\right)=0, \mathrm{d}\left(V^1+V^2+V^R\right)=0$



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$$0=\left(T^1-T^R\right)\mathrm{d}S^1+\left(T^2-T^R\right)\mathrm{d}S^2-\left(p^1-p^R\right)\mathrm{d}V^1-\left(p^2-p^R\right)\mathrm{d}V^2$$

- Equilibrium implies $T^1=T^2=T^R=T, \qquad p^1=p^2=p^R=p$
- Now consider the $1+2$ subsystem, and remember that $\mathrm{d}G=\mathrm{d}\left(E-TS+pV\right)$. With the T and p constraint

$$0=\mathrm{d}E_1+\mathrm{d}E_2+\mathrm{d}E^R=\mathrm{d}E_1+\mathrm{d}E_2+T\mathrm{d}S^R-p\mathrm{d}V^R=$$

$$=\mathrm{d}\left(E_1+E_2\right)-T\mathrm{d}\left(S_1+S_2\right)+p\mathrm{d}\left(V_1+V_2\right)=\left(\mathrm{d}\left(G_1+G_2\right)\right)_{T,p}$$

Maxwell relations

- Considering double derivatives of thermodynamic potentials reveals relations between macroscopic quantities

$$\frac{\partial^2 E}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_S, \qquad \frac{\partial^2 E}{\partial S \partial V} = -\left(\frac{\partial p}{\partial S}\right)_V \rightarrow \boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V}$$

- Similar equations hold for the other potentials

$$\frac{\partial^2 H}{\partial S \partial p} \rightarrow \boxed{\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p}$$

$$\frac{\partial^2 A}{\partial T \partial V} \rightarrow \boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V}$$

$$\frac{\partial^2 G}{\partial T \partial p} \rightarrow \boxed{-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p}$$

Constrained derivatives of a function

- Consider a function $z = z(x, y)$

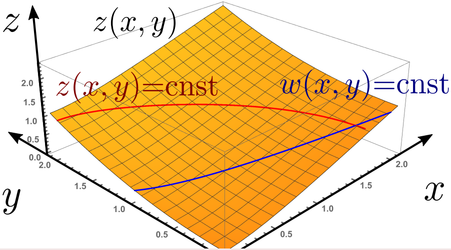
$$\mathrm{d}z = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y$$

  - If one requires constant z, the relation between the differentials is

$$\left(\frac{\partial y}{\partial x}\right)_z = -\left(\frac{\partial z}{\partial x}\right)_y \Big/ \left(\frac{\partial z}{\partial y}\right)_x \quad \rightarrow \quad \left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

- Now consider a derivative along another constraining function $w = w(x, y)$

$$\mathrm{d}z = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_w \mathrm{d}x \quad \rightarrow \quad \left(\frac{\partial z}{\partial x}\right)_w = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_w$$



Specific heat(s)

1. Recall definitions of heat capacity (e.g. $(\mathrm{d}E)_V = T\mathrm{d}S = C_V\mathrm{d}T$)

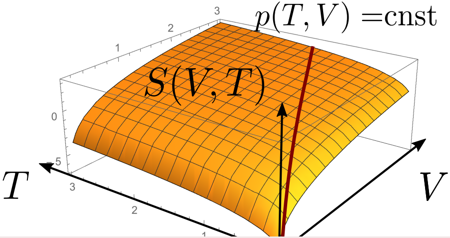
$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\partial E}{\partial S}\right)_V \left(\frac{\partial S}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V ; \; C_p = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

2. Take $S = S(T, V)$ and move along a constant-p line

$$(\mathrm{d}S)_p = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T (\mathrm{d}V)_p = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T$$

3. This provides a relation between the heat capacities, the isothermal compressibility and the thermal expansion coefficient

$$\frac{C_p - C_V}{T} = \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial p}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial T}\right)_p\right]^2$$



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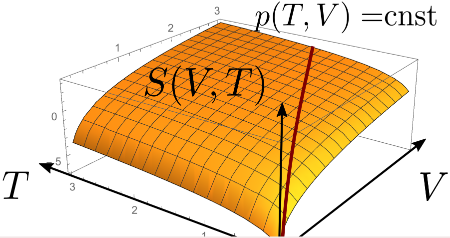

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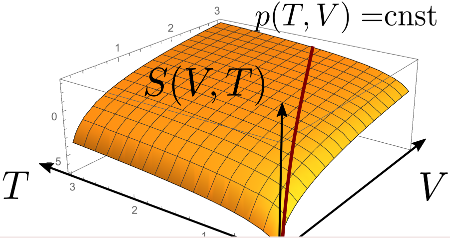

Euler's Theorem for homogeneous functions

- A function is said to be homogeneous of degree *n* if

$$f\left(\lambda x_1, \lambda x_2, \ldots \lambda x_m\right) = \lambda^n f\left(x_1, x_2, \ldots x_m\right)$$

  - Take the λ-derivative of both sides

$$\sum_i f_i'\left(\lambda x_1, \lambda x_2, \ldots \lambda x_m\right) x_i = n\lambda^{n-1} f\left(x_1, x_2, \ldots x_m\right)$$

  - For $\lambda = 1$

$$\sum_i x_i \frac{\partial f}{\partial x_i}\left(x_1, x_2, \ldots x_m\right) = nf\left(x_1, x_2, \ldots x_m\right)$$

Gibbs-Duhem equation

- The energy is a homogeneous function of S, V, n_i so

$$E(S,V,n_i)=\frac{\partial E}{\partial S}S+\frac{\partial E}{\partial V}V+\sum_i\frac{\partial E}{\partial n_i}n_i=TS-pV+\sum_i\mu_i n_i$$

  - From the definition of Gibbs free energy, $G(T,p,n_i)=E-TS+pV=\sum_i\mu_i n_i$

- The total differential of E is

$$\mathrm{d}E=T\mathrm{d}S+S\mathrm{d}T-p\mathrm{d}V-V\mathrm{d}p+\sum_i\left[\mu_i\mathrm{d}n_i+n_i\mathrm{d}\mu_i\right]$$

  but we know that the differential of E reads

$$\mathrm{d}E=T\mathrm{d}S-p\mathrm{d}V+\sum_i\mu_i\mathrm{d}n_i$$

  so

$$\boxed{S\mathrm{d}T-V\mathrm{d}p+\sum_i n_i\mathrm{d}\mu_i=0}\qquad\text{Gibbs-Duhem equation}$$

Multi-phase equilibrium

- Consider an isolated system containing P phases ans M component. Each phase can be seen as a subsystem, and the interface terms ignored.

$$\delta E = \sum_{i=1}^{P} \delta E_i = \sum_{i=1}^{P} T^i \delta S^i - p^i \delta V^i + \sum_{j=1}^{M} \mu_j^i \delta n_j^i$$

- Being an isolated system, several conservation constraints must be enforced

$$\sum_i \delta S^i = 0, \quad \sum_i \delta V^i = 0, \quad \sum_i \delta n_j^i = 0$$

- The only way to guarantee $\delta E \geq 0$ (minimum energy principle) for any value of the changes in the $\delta\cdot$

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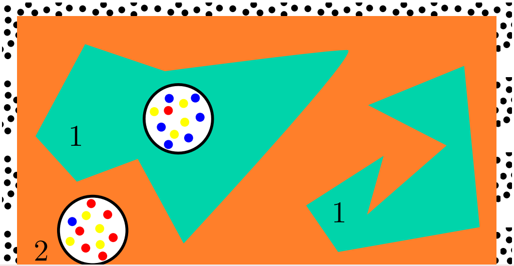

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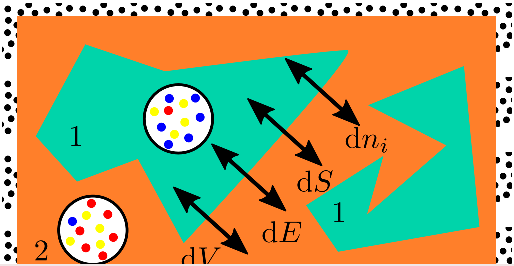

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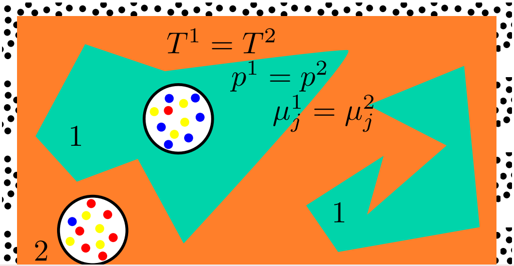


Chemical potential and mass transport

- Consider a situation with $\mu_j^1 > \mu_j^2$. The system is out of equilibrium, and the spontaneous direction of evolution is that such that $\Delta E < 0$. At constant T and p throughout the system the only non-zero term in the energy differential will be

$$\mu_j^1 \Delta n_j^1 + \mu_j^2 \Delta n_j^2 < 0$$

- Mass balance implies $\Delta n_j^2 = -\Delta n_j^1$, i.e.

$$\left(\mu_j^1 - \mu_j^2\right) \Delta n_j^1 < 0$$

- For $\mu_j^1 > \mu_j^2$ this implies $\Delta n_j^1 < 0$, i.e. components flow from the phase with higher chemical potential to that with lower μ.

Conditions for stable equilibrium

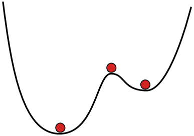
- Take a system in equilibrium, for which $\delta E = 0$. Then, one has to check whether the second-order variation is positive, $\delta^2 E \geq 0$
- Considering an isolated system, with two subsystems that can only exchange heat, one gets

$$0 \leq \frac{\partial^2 E^1}{\partial \left(S^1\right)^2} \left(\delta S^1\right)^2 + \frac{\partial^2 E^2}{\partial \left(S^2\right)^2} \left(\delta S^2\right)^2 = \left(\frac{\partial^2 E^1}{\partial \left(S^1\right)^2} + \frac{\partial^2 E^2}{\partial \left(S^2\right)^2} \right) \left(\delta S^1\right)^2$$

  - Considering $\left(\partial^2 E/\partial S^2\right)_{V,n} = (\partial T/\partial S)_{V,n} = T/C_V$, and that $T_1 = T_2$ because of equilibrium,

$$\left(\frac{T}{C_V^1} + \frac{T}{C_V^2} \right) \geq 0$$

that implies $T/C_V \geq 0$ since one could take any arbitrary subsystem



Generalized equilibrium conditions

- Consider a thermodynamic potential Φ (any of E, H, A, G) that depends on some extensive variables X and some intensive variables u, z. Take x to be the variable conjugate to X, i.e. $x = \partial\Phi/\partial X$. Then the second-order differential will be e.g.

$$0 \le \left[\frac{\partial^2\Phi^1}{\partial\left(X^1\right)^2} + \frac{\partial^2\Phi^2}{\partial\left(X^2\right)^2}\right]\left(\delta X_1\right)^2 + \dots$$

- The positivity condition has to apply to each term separately, so we don't need to consider the terms in the differential containing other extensive variables.
- Taking into account the possibility of arbitrarily subdividing the system - so the conditions is not specific to subsystem 1 or 2 - one gets conditions of the form

$$\frac{\partial^2\Phi}{\partial X^2} = \frac{\partial x}{\partial X} \ge 0$$

Molar quantities and molar fractions

- Often one wants to refer to the properties of a system independently of its absolute size.
- It is then possible to introduce "molar" quantities, e.g.
  - Molar volume, $v = V/n$
  - Molar fractions $x_i = n_i/n$ (defining $n = \sum_i n_i$)
  - Molar thermodynamic potentials, e.g. molar Gibbs free energy $g = G/n$ (NB: $g \equiv \mu$!)
- If derivatives are done at constant system size, there are similar relationships between extensive and molar quantities, e.g.

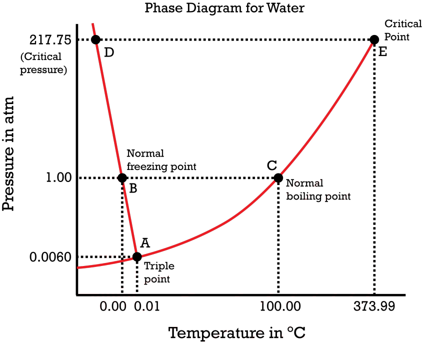
$$\left(\frac{\partial \mu}{\partial p}\right)_T = \frac{1}{n}\left(\frac{\partial G}{\partial p}\right)_T = \frac{V}{n} = v$$

$$\left(\frac{\partial \mu}{\partial T}\right)_p = \frac{1}{n}\left(\frac{\partial G}{\partial T}\right)_p = -\frac{S}{n} = -s$$

Gibbs Phase Rule

- Consider a system with M components and P phases, described in terms of intensive variables - p, T and M molar fractions $x_j^i = n_j^i / \sum_j n_j^i$
- Equilibrium between the different phases implies $M(P-1)$ equations connecting the chemical potentials, $\mu_j^i = \mu_j^{i'}$, plus P equations connecting the molar fractions within each phase ($\sum_j x_j^i = 1$)
- This leaves a number of independent degrees of freedom f which is

$$f = 2 + MP - P - M(P-1) = 2 + M - P$$



Phase transitions and phase lines

- A phase line separates the stability range of two phases. Determined by

$$\mu_1(p, T) = \mu_2(p, T)$$

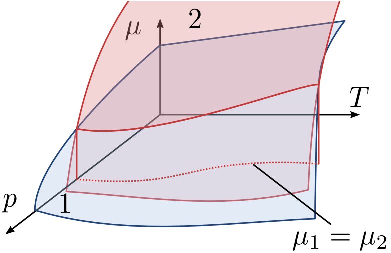
  - The properties of the system may have a discontinuity (1st-order phase transition)

$$v_1 - v_2 = \left(\frac{\partial \mu_1}{\partial p}\right)_T - \left(\frac{\partial \mu_2}{\partial p}\right)_T$$

  At critical points the two surfaces can be tangent, so it is possible not to have a discontinuity (second-order phase transition)

- We can compute the slope of coexistence line (Clausius-Clapeyron eqn.)

$$\frac{\partial p}{\partial T} = -\left(\left(\frac{\partial \mu_1}{\partial p}\right)_T - \left(\frac{\partial \mu_2}{\partial p}\right)_T\right)^{-1}\left(\left(\frac{\partial \mu_1}{\partial T}\right)_p - \left(\frac{\partial \mu_2}{\partial T}\right)_p\right) = \frac{s_1 - s_2}{v_1 - v_2}$$



Entropy derivatives

- Derivatives of *E* and *S* are related due to the fundamental relation $S\,(E, V)$