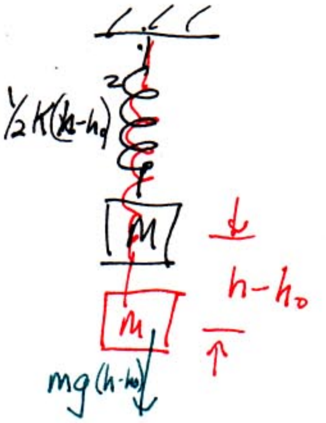
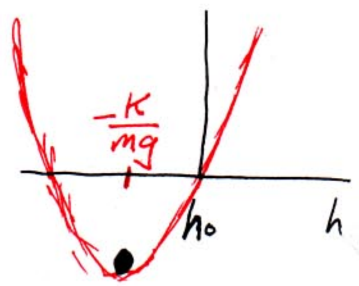
Free Energy Minimization





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Mass hangs on end of spring.

How far does the spring stretch?

$$K(h-h_0) = -mg$$

Systems deform to <u>minimize</u> their <u>energy</u>. ??

What principle of physics is that? Energy is <u>conserved</u>, not minimized.

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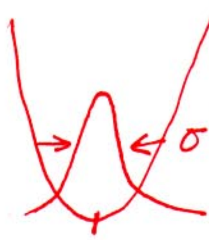


$$\sigma^2 = \langle (h-h^*)^2 \rangle$$

$$h^* = h_0 - \frac{K}{mg}$$

Energy is (mostly) lost to heat bath: shared "equally" with 6N atomic degrees of freedom.

Lost to heat.

Fluctuations: Equipartition Theorem

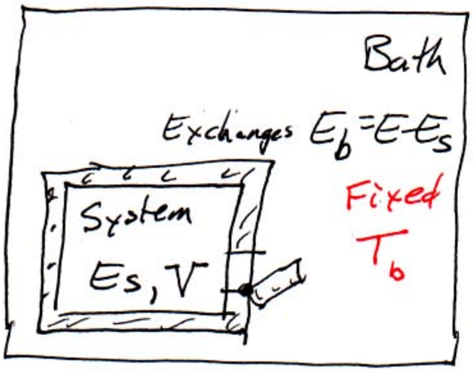
$$\left\langle \tfrac{1}{2}K(h-h^*)^2 \right\rangle = \tfrac{1}{2}k_B T$$

$$(h-h^*)^2 = \frac{\tfrac{1}{2}k_B T}{\tfrac{1}{2}K} = \frac{4\times10^{-21}\,J}{K}$$

Energy E is minimized up to <u>thermal</u> <u>fluctuations</u>

$$K \sim 10\,N/m \Rightarrow \sqrt{(h-h^*)^2} = \sigma = 2\times10^{-11}\,m = 0.2\,\text{Å}.$$

Is there a more general principle? Suppose our "system" is more complex than a mass on a spring? Entropy of system is also important.



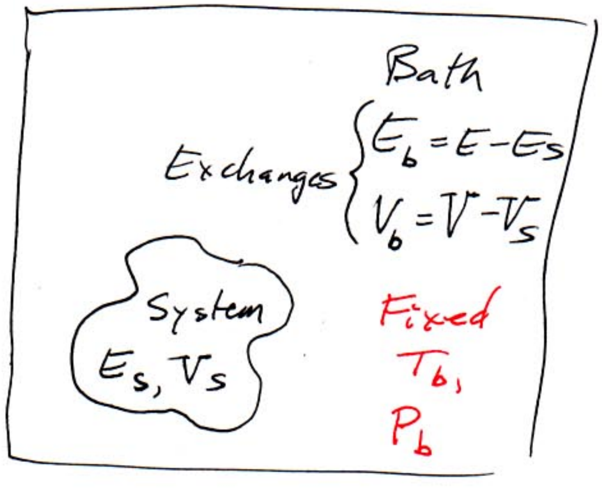
System might be piston of fixed volume V, N atoms, stealing/exchanging energy E_s from bath, at fixed temperature T_b

Minimize Helmholtz Free Energy $F(T_b, V)$

System might be chemical reaction

$2H_2 + O_2 \leftrightarrow 2H_2O$

at fixed pressure P_b, (or melting of ice...)



Minimize Gibbs Free Energy $G(T_b, P_b)$

Can we guess formulas for F, G?

Fundamental Principle: <u>Entropy of Universe is Maximized.</u> What function of system energy E_s and entropy S_s is <u>minimized</u>?

- Won't derive it. (Partition functions, canonical ensembles, ...) Could do a hokey job.

$$F = E - TS$$ Helmholtz free energy.

- As $T \to 0$, all energy is extracted from system! minimizing F minimizes E becase they agree. Entropy is increasingly important at higher T.
- Does minimizing F maximize entropy for the universe?

$$F = E_s - T_b\, S_s(E_s)$$

$$\frac{\partial F}{\partial E_s} = 1 - T_b \underbrace{\frac{\partial S_s}{\partial E_s}}_{1/T_s} = 1 - T_b / T_s = 0$$

if $T_s = T_b$

More directly,

$$\frac{1}{T_s} = \frac{\partial S_s}{\partial E_s} = \frac{1}{T_b} = \frac{\partial S_b}{\partial E_b} = -\frac{\partial S_b(E - E_s)}{\partial E_s}$$

So total $S_s + S_b$ at an extremum. ✓

- Why is F not a function of E_s?

Math: $\frac{\partial F}{\partial E_s} = 0$ after it's minimized, so F doesn't involve E_s.

Legendre Transform: $F(T,V) = E(V) - TS(E,V)$

Changes independent variables from $(E,V) \to (T,V)$

- Does F substitute for E in otherways?

Example: Pressure in the ideal gas

$E = \frac{3}{2} k_b T$ (monotomic ideal gas).

$\frac{\partial E}{\partial V} = 0$ (energy not dependent on volume! $P \neq -\frac{\partial E}{\partial V}$!)

FIX

$F = E - TS = \frac{3}{2} N k_b T - T\, k_b \log(\Omega_x \cdot \Omega_P)$

$= \frac{3}{2} N k_b T - T k_b N \log V - T k_b \log(1/N!)$

$\frac{\partial F}{\partial V} = -\frac{T k_b N}{V} = -\frac{N k_b T}{V} = -P$ ✓

$$\boxed{P = -\frac{\partial F}{\partial V}\Big|_{T,N}}$$ General formula

- Systems at constant temperature, pressure minimize <u>Gibbs</u> free energy

$$G = E - TS + PV$$

$$= E_s - T_b S_s + P_b V_s$$

- Minimizing G with respect to volume equalizes pressure

$$\frac{\partial G_s}{\partial V_s} = \frac{\partial}{\partial V_s}\left(F(T_b, V_s) + P_b V_s \right)$$

$$= \frac{\partial F_s}{\partial V_s} + P_b$$

$$= -P_s + P_b \rightarrow$$ Extremized (minimum) when Pressures equal

- Gibbs free energy independent of V, independent variables P, T

$$G(T_b, P_b) = \underbrace{F(T_b, V_s) + P_b V_s}_{\text{Understood that minimized wrt } V_s}$$