Review

Isothermal system

\[ d(E - TS) = -PdV + xdx. \]

\( A \equiv E - TS \) is convenient.

\[ \Delta A \leq W \]

Free energy minimum principle

Convex Analysis

\[ A = \inf_S \{E - TS\} \]

Legendre transformation in convex analysis

\[ -A = \sup_S \{ST - E\} \]

inverse transformation

\[ E = \sup_T \{ST - (-A)\} \]
Use of Jacobian 24.9-24.12

\[
\left( \frac{\partial A}{\partial B} \right)_C = \frac{\partial (A, C)}{\partial (B, C)}
\]

\[
\PD{A}{B}{C} = \pder{(A,C)}{(B,C)}
\]

Sign rule

Calculus becomes Algebra

\[
\frac{\partial (A, B)}{\partial (C, D)} = \frac{\partial (A, B)}{\partial (X, Y)} \frac{\partial (X, Y)}{\partial (C, D)}.
\]

Maxwell’s relations

\[
\frac{\partial (X, x)}{\partial (y, Y)} = 1.
\]
Lect 10. **Intro to SM + Jacobian, Information**

Jacobian Review: entropic elasticity — rubber band

Recall entropic force

\[ L \uparrow \Rightarrow S \downarrow \text{ (under a given } T) \]

\[
\left( \frac{\partial S}{\partial L} \right)_T < 0.
\]

How can we experimentally demonstrate this?

\[
0 > \frac{\partial(S, T)}{\partial(L, T)} = \frac{\partial(S, T) \partial(L, S)}{\partial(L, S) \partial(L, T)}
\]

\[
= - \left( \frac{\partial T}{\partial L} \right)_S \left( \frac{\partial S}{\partial T} \right)_L = - \frac{C_L}{T} \left( \frac{\partial T}{\partial L} \right)_S.
\]

We can confirm:

\[
\left( \frac{\partial T}{\partial L} \right)_S > 0
\]
\[
\left( \frac{\partial T}{\partial L} \right)_S > 0
\]
gives adiabatic cooling.

How about
\[
\left( \frac{\partial F}{\partial T} \right)_L
\]?

\[
\left( \frac{\partial L}{\partial T} \right)_F
\]?
Statistical Mechanics

Why we need it. 17.2
What we really need: Translation table 17.3
   cf LLN we do not need distributions

thermodynamic coordinate: mechanical
entropy: Boltzmann’s principle 17.4

\[ S = k_B \log w(E, X). \]

# of states compatible with macrostate \((E, X)\). 17.5
The rest is taken care of by Thermodynamics. 17.6

THE END

We do not need

Principle of equal probability
The rest is technical???

Big issue
How can we define $\tilde{w}(E, X)$?

Generally, $H$ and $\hat{X}$ are not commutative.

von Neumann 1939 assumed $\exists$ commutative approximation.

Still a hot topic
BIT
Entropy and information 15.7-10

1 bit/molecule = $9.57 \times 10^{-24}$ J/K·molecule

= $5.7628$ J/K·mol = $1.377$ cal/K·mol 21.12
Relation between Thermodynamics and statistical mechanics

Principle of equal probability: this CANNOT be a microscopic statement

Derivation of Boltzmann’s principle (following Einstein)