Review of statistical thermodynamics:

Thermodynamics = statistical mechanics, "bulk" properties of a system
- laws of thermodynamics express macroscopic effects of interactions
- the laws apply close to equilibrium and are independent of the initial history of the system

Laws of thermodynamics follow from relations between the bulk properties and the underlying dynamics of the system.

The basic principle of statistical mechanics: A canonical ensemble.

For a system in equilibrium, which can be in one of many states, the probability that the system has exactly \( E_n \) is

\[
\frac{1}{Z} e^{-E_n/kT} = \frac{N!}{n_1! n_2! \ldots} e^{-E_1/kT} e^{-E_2/kT} \ldots
\]

Boltzmann constant

Further discussion:

If \( |\psi\rangle \) is a state of every \( E_i \) and \( A \) is an operator, then expected value is
$$\langle A \rangle = \frac{1}{Z} \sum_i \langle i | A | i \rangle e^{-E_i / kT}$$

All subsequent laws follow. We can first try to understand where all this comes from.

Let the microcanonical ensemble equal partition $\Rightarrow$

Probability of fixed energy $\Rightarrow$ number of available states.

Consider a system $S$ in equilibrium with a heat bath $H$.

$$S \quad H$$

$E_i \quad H_i$

Every levels $\leftarrow$

- Every levels of $H$ are quasi-continuous
- $H_i \gg E_j$ for all $i, j$
\[ \gamma(H_r) = \text{dimension of stable + unstable} \]

\[ \gamma(H_r) \delta = \# \text{ of states in the vicinity of } H_r \pm \delta \]

\[ \Rightarrow \text{microcanonical ensemble } E_0 = H_r + E_r \]

\[ P(E_r) \propto \gamma(E_0 - E_r) \delta \]

\[ \begin{align*}
\alpha & = \frac{P(E_r)}{P(E_s)} = \frac{\gamma(E_0 - E_r)}{\gamma(E_0 - E_s)} \ln \frac{\gamma(E_0 - E_r)}{\gamma(E_0 - E_s)}
\end{align*} \]

and to \( E \ll E_r \)

\( \star \) Now assume \( \frac{d}{dE} \ln \gamma(E) = \beta / E \) is almost constant for \( E \) in the region under consideration, then

\[ \frac{P(E_r)}{P(E_s)} = e \]

\( \star \) This follows from the assumption that if

Thus a quasi uniform spectrum and no characteristic energy \( \Rightarrow \) just like 100 for variable delay \( \Rightarrow \) no fixed delay

\[ \frac{d\gamma}{dE} \propto -\gamma(E) \]
If there is no charged in energy $E$, slit every

\[ \frac{\eta(E_1 + E_0)}{\eta(E_1)} = \eta(E_0) = \frac{d\eta}{dE} \frac{E_1}{E_1 + E_0} \]

Illustrations: take the heat both to be a system

on $N$ particles in the box:

The energy of $N$ is:

\[ F = \frac{1}{2m} \sum_{i=1}^{N} \frac{p_i^2}{2} + \frac{1}{2m} \sum_{i=1}^{N} \frac{p_i^2}{2} \]

with periodic boundary condition.

\[ p_i = \frac{2\pi n_i}{L} \]

\[ F = \frac{(2\pi)^2}{2mL} \sum_{i=1}^{N} \frac{q_i^2}{2} \]

the number of states with energy less than $F$ is value

of a sphere in $3N$ dimensions

\[ R = \sqrt{F} \]

\[ \Rightarrow \# \text{ of state with energy } \leq (F) \leq \frac{3N}{2} \]

\[ \Rightarrow \eta(F) \leq \frac{3}{2} \]

\[ \Rightarrow \frac{d}{dF} \ln \eta(F) = \frac{3N}{2F} = \frac{3}{2} \left( \frac{F}{N} \right) = \frac{1}{2} \text{ every particle} \]
Consider two independent systems $S_A$ and $S_B$.

The probability of $S_A$ losing every $A_i$ is

$$P_A(A_i) = \frac{1}{\mathcal{E}_A} e^{-\mathcal{E}_A}$$

Place $S_A$ and $S_B$ in contact and consider combined system $S_T = S_A + S_B$ with every $T_k = A_i + B_j$.

$$\Rightarrow P_T(T_k) = P_T(A_i + B_j) = \frac{e^{-\mathcal{E}_T(A_i + B_j)} - \mathcal{E}_T A_i - \mathcal{E}_T B_j}{\mathcal{E}_A \mathcal{E}_B} = \frac{e^{-\mathcal{E}_T A_i} - \mathcal{E}_T A_i - \mathcal{E}_T B_j}{\mathcal{E}_A \mathcal{E}_B}$$

The probability that $S_T$ is such that $S_A$ wins every $A_i$ is

$$P_T(A_i) = \frac{e^{\mathcal{E}_T A_i}}{\mathcal{E}_T} = \frac{e^{-\mathcal{E}_T B_j}}{\mathcal{E}_B} = \frac{e^{\mathcal{E}_T A_i}}{2\mathcal{E}_A} = P_A(A_i)$$

Similarly, $P_B(B_j) = \frac{e^{-\mathcal{E}_T B_j}}{2\mathcal{E}_B}$.

In equilibrium, the two systems have the same $p$ $\Rightarrow$ temperature.

In the same manner, so it is convenient to think of

$$p = \frac{1}{kT} \quad (\Rightarrow \text{ constant})$$
Now let's see how the equilibrium follows from the definitions.

Define $F = \text{Helmholtz free energy}$:

$$ Z = \sum_u e^{-\epsilon_u/kT} = e^{-F/kT} $$

$$ F = -kT \ln Z = -kT \ln \left( \sum_u e^{-\epsilon_u/kT} \right) = \mathcal{F} = \mathcal{F}(V, T) $$

$S$ = entropy is defined as $-k \sum_u p_u \ln p_u$

$$ p_u = \frac{1}{Z} e^{-\epsilon_u/kT} $$

We then have:

$$ -\left( \frac{\partial F}{\partial T} \right)_V = kT \frac{1}{Z} \frac{\partial Z}{\partial T} $$

$$ = kT \left[ \ln Z + \frac{1}{Z} \sum_u \epsilon_u e^{-\epsilon_u/kT} \right] $$

$$ = S $$

$$ P = \text{pressure} = \sum_u \left( -p_u \frac{\partial \epsilon_u}{\partial V_{\text{other}}} \right) = -\left( \frac{\partial F}{\partial V} \right)_T $$

$$ V = \text{average energy} = \frac{1}{Z} \sum_u \epsilon_u e^{-\epsilon_u/kT} $$

$$ \text{mim} \quad \frac{\partial T}{\partial T} = \frac{1}{kT} \sum_u \epsilon_u e^{-\epsilon_u/kT} = -\frac{\partial}{\partial T} \left( \frac{2F}{kT} \right) $$

$$ = \delta \left( \frac{\partial}{\partial T} \right) \left( \frac{\epsilon}{T} \right) $$
Since \( S = -2F \frac{\partial F}{\partial T} \), \( \Rightarrow U = F + TS \)

Specific heat \( \Rightarrow \left( \frac{2U}{\partial T} \right)_V = -T \left( \frac{2F}{\partial T} \right)_V \)

\( \Rightarrow S = -\left( \frac{2F}{\partial T} \right)_V \) holds at equilibrium when \( F \) is defined.

Now how equilibrium \( S \) always increases with \( F \) due to show that?

Given canonical ensemble \( \Rightarrow \) for systems with both energy and particle numbers:

Heat \( \Rightarrow \) derivative analogous to the canonical ensemble:

\[ \mathbb{Z}_G = \frac{1}{N} \sum_{\{\phi\}} e^{-\beta (E_\phi - \mu N)} \]

\( \beta \) states at \( \mu \) given \( N \)

\( \Rightarrow \) grand potential:

\[ Z_G = e^{-\beta U} \quad V_G = -\beta T \ln Z_G \]

\[ \mathcal{U} = \mathcal{S}(V, T, \mu) \]

So:

final answer
\[
\frac{1}{\epsilon_0} \left( \frac{\partial \rho}{\partial t} \right)_{\mu \nu} = \frac{1}{\epsilon_0} \frac{1}{k T^2} \sum_{j=1}^{N} \left( \epsilon_j - \mu N \right) e^{\frac{-\epsilon_j}{k T}}
\]

\[
= \frac{1}{k T} \left( N - \mu N \right)
\]

- \left( \frac{\partial \rho}{\partial t} \right)_{\mu \nu} = \kappa \text{ln} \epsilon_0 + \frac{\kappa T}{\epsilon_0} \left( \frac{\partial \phi}{\partial t} \right)_{\mu \nu}
\]

\[
\epsilon T^2 \left( \frac{\partial \phi}{\partial t} \right)_{\mu \nu} = N - \mu N = T \left( \frac{\partial \rho}{\partial t} \right)_{\mu \nu} + \Delta \rho
\]

\[
\Delta \rho = N - T \left( \frac{\partial \phi}{\partial t} \right)_{\mu \nu} - \mu N
\]

\[
\text{also: } \left( -\frac{\partial \rho}{\partial \mu} \right)_{\mu \nu} = \kappa T \frac{1}{\epsilon_0} \left( \frac{\partial \phi}{\partial \mu} \right)_{\mu \nu} = \kappa T \nabla N - N
\]

Finally \( \Delta \rho = \nabla \left( \phi \mu \nu \right) = \nabla T S - \mu N \)

\[
S = -\left( \frac{\partial \phi}{\partial t} \right)_{\mu \nu} \quad \text{and} \quad N = -\left( \frac{\partial \rho}{\partial \mu} \right)_{\mu \nu}
\]

We can rewrite \( \Delta \rho \) as a function of its independent variables: \( \rho, \mu, T \) by taking advantage of the following:

- The dependent variables: \( N, \rho, T \)

\[
\rho = -\left( \frac{\partial \phi}{\partial \mu} \right)_{\mu \nu}
\]
Legendre transformations \( \rightarrow \) go to new, independent variables.

\[ E = E(S, V, N) \quad dE = TdS - pdV + \mu dN \]

Helmholtz free energy:

\[ F = E - TS \]
\[ dF = -SdT - pdV + \mu dN \]
\[ F = F(T, V, N) \]

Gibbs free energy:

\[ G = E - TS + pV \Rightarrow dG = -SdT + Vdp + \mu dN \]
\[ G = G(T, p, N) \]

Thermodynamic potential

\[ \mathcal{R} = E - TS - \mu N \Rightarrow d\mathcal{R} = -SdT - pdV - \mu dN \]
\[ \mathcal{R} = \mathcal{R}(T, p, \mu) \]
Examples of correlation $\hat{\mathcal{G}}$:

Define $\hat{P} = \frac{1}{Z} e^{-\beta \hat{H}}$, $\hat{E} = \hat{H} - \mu \hat{N}$

Grand canonical Hamiltonian

$Z = \sum_{N} e^{-\beta (\mathcal{E} + \mu \hat{N})} = \sum_{N} \langle N | e^{-\beta \hat{E}} | N \rangle$

$= TV e^{-\beta \mu} \Rightarrow \lim_{TV} Z = 1$

and for observables: $\langle \hat{A} \rangle = TV \langle \hat{P} \hat{A} \hat{P} \rangle = \frac{TV \langle e^{\beta \hat{A}} \hat{P} \rangle}{TV \langle e^{-\beta \hat{E}} \hat{P} \rangle}$

In a finite system only values of $N$ matter

Contributions to $\sum_{N}$ will be peaked around an average value $\bar{N}$. We therefore compute $\mathcal{P}$ as a function of $\mu$ and at the end of the calculation set $\mu$ to give the derived (observed) value of $\bar{N}$ or $\bar{N}/V = \mu$ (just like we did when discussing superconductivity).