Isothermal system

\[ Z = T r e^{-\beta E} = \sum_{E} w(E) e^{-\beta E}. \]

\[ A = -k_B T \log Z. \]

Recall the ‘honest’ Legendre transformation (16.9-11):

\[ -A = \sup_{S} \{ST - E\}. \]

Notice that

\[ w(E) e^{-\beta E} = e^{\beta(TS - E)} \]

for each \( E \) value \( S(E) \) may be realized as an equilibrium value with appropriate constraints.

\[ \max_{E} w(E) e^{-\beta E} = \max_{S} w(E) e^{-\beta E} = e^{-\beta A}. \]
\[ PV = \sup_{S,N} \{ST + \mu N - E\}. \]

cf.

\[ E = TS - PV + \mu N + xX. \]

Grand canonical ensemble:

\[
\begin{align*}
\sup_{S,N} e^{-\beta(E-ST-\mu N)} &= \sum w(E, N) e^{-\beta E + \beta \mu N} \\
&= \sum Z(T, N) e^{\beta \mu N} = \Xi,
\end{align*}
\]

or

\[ PV = k_B T \log \Xi. \]

Open system, **BUT** if \( \log N/N \ll 1 \) OK!
Lecture 12 Elements of ensemble theory

Let us quickly review elementary examples.

Let us follow Sect 18
∗ Schottky defects 18.1-18.2
∗ Stirling’s, Gosper’s formula 18.3
∗ Schottky type specific heat—energy gap
∗ Schottky via canonical, binomial theorem 18.8
∗ All the state $\to$ factorization 18.9
∗ Schottky: micro-c comparison 18.10

∗ Frenkel defects 18.11
∗ Frenkel: micro-c equivalence 18.12
∗ Frenkel by micro 18.13

Large deviation basic: why 18.15

$$P(S_N/N \sim x) \approx e^{-NI(x)}?$$
**Density operator** 19.3

If we assume the principle of equal probability, we can estimate the probability of a set of microstates.

Classic counterpart: 19.6

Can we use it microscopically? 19.7 NO.
Second Law and Statistical Mechanics

Liouville’s theorem

Jarzynski’s equality

Can it be a proof of the second law?

Lenard’s theorem

Classical case, Gibbs paradox
Information thermodynamics
Variational principle