8.333 Fall 2025 Recitations 7: Ensemble/thermo recap

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These notes are largely a conglomeration of the previous years' recitation notes by Julien Tailleur, Amer Al-Hiyasat, and Sara Dal Cengio.

For a more comprehensive resource, see Ch. 1 and 4 of Mehran Kardar's *Statistical Physics of Particles.*

Contents

1 Introduction

In class, we have studied the microcanonical ensemble, with fixed (E, V, N). We have also studied the canonical (or isothermal) ensemble, with fixed (T, V, N). Finally, we have studied the grand canonical ensemble, with fixed (T, V, μ). In this recitation, we will go over the **isobaric/isothermal ensemble**, sometimes called the **Gibbs canonical ensemble**, which has fixed (T, P, N).

The ensembles are summarized in the following table, which gives the variables that are fixed in each ensemble. Intensive variables are colored in purple, and extensive ones in blue.

Ensemble	Fixed E or T?	Fixed V or P?	Fixed N or μ?
Microcanonical	E	V	N
Canonical	T	V	N
Grand canonical	T	V	μ
Isobaric, isothermal	T	P	N

The ensembles are also illustrated in Fig. 1.

Remark 1.1: Why no (T, P, μ) ensemble?

Why is there no (T, P, μ) ensemble? The answer is that if all extensive quantities were free to vary, there would be nothing to constrain their averages. A gas which can exchange volume, energy, and particles with a reservoir has nothing constraining its scale.

In fact, there is no reason why such a system would remain much smaller than the reservoir. This is one of the central assumptions used in our derivations.

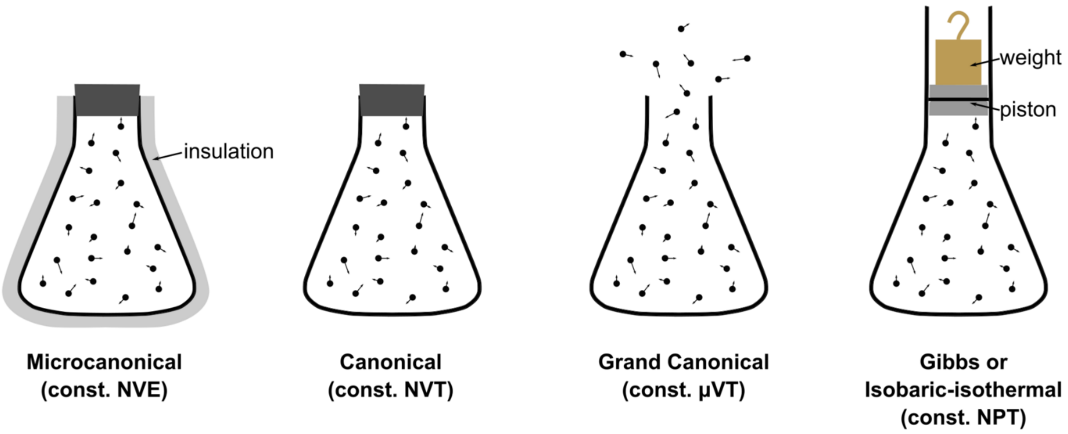

Figure 1: Statistical ensembles. https://en.wikipedia.org/wiki/Ensemble_(mathematical_physics)

2 Ensemble theory recap: isobaric, isothermal

We will now review ensemble theory by working out the isobaric/isothermal ensemble.

2.1 Microcanonical to isobaric, isothermal

As before, consider an overall system in the microcanonical ensemble, with a fixed total $E_{\text{tot}}, V_{\text{tot}}, N_{\text{tot}}$. As in the canonical ensemble, we will divide the system into a "subsystem" with a fixed number N of particles, and much larger "reservoir" with $N_r = N_{\text{tot}} - N$ particles. The system can still exchange heat with the reservoir, but now suppose it can also exchange volume. For instance, it may be connected to the reservoir through a piston, as illustrated in Fig. 2.

Denote the subsystem states as φ, with energy $E(\varphi)$ and volume $V(\varphi)$. Denote the reservoir states as φ_r with energy $E_r(\varphi_r)$ and volume $V_r(\varphi_r)$. Suppose the overall state $\varphi_{\text{tot}} = \varphi \otimes \varphi_r$ has energy $E_{\text{tot}}(\varphi_{\text{tot}}) = E(\varphi) + E_r(\varphi_r)$ and volume $V_{\text{tot}}(\varphi_{\text{tot}}) = V(\varphi) + V_r(\varphi_r)$. (This additivity requires that, for instance, the system boundaries are small relative to its bulk.)

For any energy E and volume V, suppose the subsystem has $\Omega(E, V, N)$ such states. Likewise for any energy E_r and volume V_r, suppose the reservoir has $\Omega_r(E_r, V_r, N_r)$ such states. Then we can say the total degeneracy Ω_{tot} of the combined systems is given by

$$\Omega(E, V, N)\Omega_r(E_r, V_r, N_r) = \Omega_{\text{tot}}(E + E_r, V + V_r, N + N_r) \; . \tag{1}$$

This is exactly true if φ and φ_r are perfectly independent, and is approximately true if the boundary of the system is small relative to its bulk.

The fundamental hypothesis of statistical mechanics implies that the probability of a state of the overall system is

$$P_{\text{tot}}(\varphi_{\text{tot}}) = \frac{\delta_{E_{\text{tot}}(\varphi_{\text{tot}}), E_{\text{tot}}} \delta_{V_{\text{tot}}(\varphi_{\text{tot}}), V_{\text{tot}}}}{\Omega_{\text{tot}}(E_{\text{tot}}, V_{\text{tot}}, N_{\text{tot}})} \; . \tag{2}$$

Then the probability of the *subsystem* being in state φ is simply the degeneracy of the resulting admissible reservoir states, divided by the total degeneracy:

$$P(\varphi) = \frac{\Omega_r(E_{\text{tot}} - E(\varphi), V_{\text{tot}} - V(\varphi), N_{\text{tot}} - N)}{\Omega_{\text{tot}}(E_{\text{tot}}, V_{\text{tot}}, N_{\text{tot}})} \; . \tag{3}$$

Let's define the entropy

$$S_{\text{tot}}(E_{\text{tot}}, V_{\text{tot}}, N_{\text{tot}}) \equiv k_B \log \Omega(E_{\text{tot}}, V_{\text{tot}}, N_{\text{tot}}) \tag{4}$$

$$S_r(E_r, V_r, N_r) \equiv k_B \log \Omega_r(E_r, V_r, N_r) \tag{5}$$

$$S(E, V, N) \equiv k_B \log \Omega(E, V, N) \; . \tag{6}$$

Furthermore, let's assume the subsystem is much smaller than the reservoir, so $E \ll E_r$ and $V \ll V_r$. Then we can write the

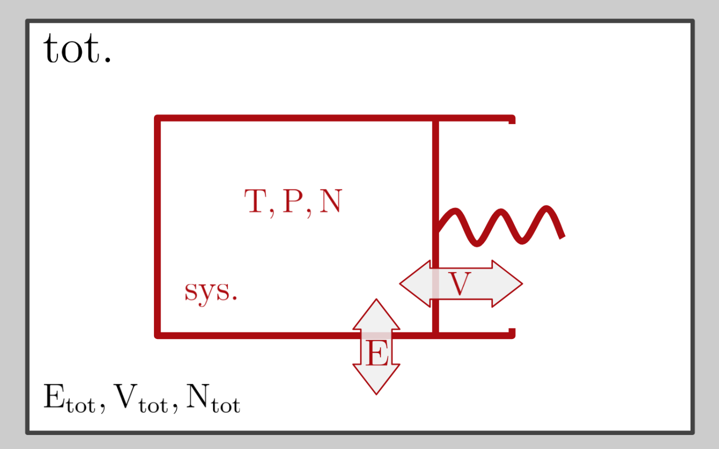

Figure 2: Moving from the microcanonical to the isobaric/isothermal ensemble. The subsystem (sys.) has fluctuating energy E and volume V, and fixed particle number N. It exchanges energy and volume with its reservoir (tot.), which has fixed energy E_{tot}, volume V_{tot}, and particle number N_{tot}.

subsystem probability (3) as

$$P(\varphi) = \exp\left[\frac{1}{k_B}\Big(S_r(E_{\text{tot}} - E(\varphi), V_{\text{tot}} - V(\varphi), N_{\text{tot}} - N) - S_{\text{tot}}(E_{\text{tot}}, V_{\text{tot}}, N_{\text{tot}})\Big)\right] \tag{7}$$

$$\approx \exp\left[\frac{1}{k_B}\Big(S_r(E_{\text{tot}}, V_{\text{tot}}, N_{\text{tot}}) - E(\varphi)\frac{\partial S_r}{\partial E_{\text{tot}}}(E_{\text{tot}}, V_{\text{tot}}, N_{\text{tot}}) - V(\varphi)\frac{\partial S_r}{\partial V_{\text{tot}}}(E_{\text{tot}}, V_{\text{tot}}, N_{\text{tot}}) - S_{\text{tot}}(E_{\text{tot}}, V_{\text{tot}}, N_{\text{tot}})\Big)\right] \tag{8}$$

$$\equiv \frac{\exp\big[-\beta E(\varphi) - \beta P V(\varphi)\big]}{Z} \, . \tag{9}$$

We have defined the inverse temperature β and the pressure P:

Definition 2.1: Temperature and pressure

Suppose a system with energy E, volume V, and particle number N is connected to a reservoir with energy $E_{\text{tot}} - E \gg E$, volume $V_{\text{tot}} - V \gg V$, and particle number $N_{\text{tot}} - N \gg N$. Suppose the reservoir has entropy S_r. We define the **temperature** of the reservoir, T, as

$$\beta = \frac{1}{k_B T} \equiv \frac{1}{k_B}\frac{\partial S_r}{\partial E_{\text{tot}}}(E_{\text{tot}}, V_{\text{tot}}, N_{\text{tot}}) \, . \tag{10}$$

We also define its **pressure** P as

$$P \equiv T\frac{\partial S_r}{\partial V_{\text{tot}}}(E_{\text{tot}}, V_{\text{tot}}, N_{\text{tot}}) \, . \tag{11}$$

We have also defined the partition function:

Definition 2.2: Partition function (isobaric/isothermal ensemble)

Consider a reservoir with entropy S_r, and a total system with entropy S_{tot}. Suppose the total system has energy E_{tot}, volume V_{tot}, and particle number N_{tot}. We define the **partition function** Z as

$$Z \equiv \exp\left[\frac{1}{k_B}\Big(S_r(E_{\mathrm{tot}}, V_{\mathrm{tot}}, N_{\mathrm{tot}}) - S_{\mathrm{tot}}(E_{\mathrm{tot}}, V_{\mathrm{tot}}, N_{\mathrm{tot}})\Big)\right] . \tag{12}$$

Note that, because the probability $P(\varphi)$ must be normalized, Z must also satisfy the following in the isobaric/isothermal ensemble:

$$Z = Z(T, P, N) = \sum_{\varphi} e^{-\beta E(\varphi) - \beta P V(\varphi)} . \tag{13}$$

We have used this equivalent definition to interpret Z as a function of T, P, and N. In this spirit, we will shift our thinking from the "subsystem/reservoir" paradigm to just a system with fixed temperature and pressure. We will no longer worry about the entropic origins of T and P (Eqs. (10)-(11)), and will instead treat them as control parameters. That's why we say that ensemble properties, such as Z, are "functions of" T, P, and N. Functions of microscopic parameters of the system, and quantities that depend on non-fixed properties of the system, will thus be given the subscript T, P, N. For instance, the probability of a state φ will now be denoted as $P_{T,P,N}(\varphi)$.

2.2 The Gibbs free energy

We are often interested in averages, such as the average energy $\langle E\rangle_{T,P,N}$ or average volume $\langle V\rangle_{T,P,N}$ of the system. For these calculations, it is useful to define the Gibbs free energy:

Definition 2.3: Gibbs free energy

In the isobaric, isothermal ensemble with partition function $Z(T, P, N)$, we define the **Gibbs free energy** $G(T, P, N)$ as

$$G(T, P, N) \equiv -k_B T \ln Z(T, P, N) . \tag{14}$$

Then, we can see that

$$\frac{1}{\beta}\frac{\partial(\beta G)}{\partial \beta}(T, P, N) = -\frac{1}{\beta}\frac{\partial}{\partial \beta}\ln Z(T, P, N) = -\frac{k_B T}{Z}\frac{\partial Z}{\partial \beta}(T, P, N) = -\frac{k_B T}{Z}\sum_{\varphi}\frac{\partial}{\partial \beta} e^{-\beta E(\varphi) - \beta P V(\varphi)} \tag{15}$$

$$= \frac{k_B T}{Z}\sum_{\varphi}\big[\beta E(\varphi) + \beta P V(\varphi)\big] e^{-\beta E(\varphi) - \beta P V(\varphi)} = \langle E\rangle_{T,P,N} + P\langle V\rangle_{T,P,N} . \tag{16}$$

Likewise,

$$\frac{\partial G}{\partial P}(T, P, N) = -\frac{k_B T}{Z}\frac{\partial Z}{\partial P}(P, T, N) = -\frac{k_B T}{Z}\sum_{\varphi}\big[-\beta V(\varphi)\big] e^{-\beta E(\varphi) - \beta P V(\varphi)} = \langle V\rangle_{P,T,N} . \tag{17}$$

2.3 Large-N limit

The probability in eq. (9) is the probability of a *microstate* φ, which contains all the detailed information about all the system's degrees of freedom. However, in large systems, we are often more interested in macroscopic properties, such as their total energy or volume. We can straightforwardly calculate the probability of having a certain energy ϵ or volume ν as follows:

$$P_{T,P,N}(\epsilon, \nu) = \sum_{\varphi:\, E(\varphi)=\epsilon,\, V(\varphi)=\nu} P_{T,P,N}(\varphi) = \sum_{\varphi:\, E(\varphi)=\epsilon,\, V(\varphi)=\nu} \frac{\exp\big[-\beta E(\varphi) - \beta P V(\varphi)\big]}{Z} \tag{18}$$

$$= \frac{\Omega(\epsilon, \nu)\exp\big[-\beta\epsilon - \beta P\nu\big]}{Z} = \frac{\exp\left[\frac{1}{k_B}S(\epsilon, \nu) - \beta\epsilon - \beta P\nu\right]}{Z} = \frac{e^{-\beta[\epsilon + P\nu - TS(\epsilon, \nu)]}}{Z} \tag{19}$$

It is useful to briefly note how fundamentally tautological this equation is. The probability of ϵ, ν is proportional to its degeneracy $e^{k_B S(\epsilon,\nu)}$. Moreover, it is also proportional to the degeneracy this ϵ, ν leaves to the reservoir, $e^{k_B S_r(E_{\mathrm{tot}} - \epsilon, V_{\mathrm{tot}} - \nu)}$.

We have, to that end, defined β and P so that $S_r(E_{\text{tot}} - \epsilon, V_{\text{tot}} - \nu) \approx -\beta\epsilon - \beta P\nu + \text{constant}$. We have made no other major assumptions.

Let's define another "free energy", this one a property of both the fixed temperature and pressure and also the fluctuating energy ϵ and volume ν.

Definition 2.4: Landau-Gibbs free energy

The **Landau-Gibbs free energy** $G^L_{T,P,N}(\epsilon, \nu)$ is defined as:

$$G^L_{T,P,N}(\epsilon, \nu) \equiv \epsilon + P\nu - TS(\epsilon, \nu)\ . \tag{20}$$

Then, we can write $P_{T,P,N}(\epsilon, \nu)$ and $Z(T, P, N)$ as

$$P_{T,P,N}(\epsilon, \nu) = \frac{e^{-\beta G^L_{T,P,N}(\epsilon,\nu)}}{Z}\ , \tag{21}$$

$$Z(T, P, N) = \sum_{\epsilon,\nu} e^{-\beta G^L_{T,P,N}(\epsilon,\nu)}\ . \tag{22}$$

Eq. (21) tells us that the most likely macrostate $\epsilon^*_{T,P,N}$, $\nu^*_{T,P,N}$ is the one that minimizes $G^L_{T,P,N}$:

$$\epsilon^*_{T,P,N},\, \nu^*_{T,P,N} = \underset{\epsilon,\nu}{\text{argmin}}\ G^L_{T,P,N}(\epsilon, \nu) = \underset{\epsilon,\nu}{\text{argmin}}\ \big[\epsilon + P\nu - TS(\epsilon, \nu)\big]\ . \tag{23}$$

Let's write these optimal ϵ, ν as *functions* of T, P, and N:

$$E(T, P, N) \equiv \epsilon^*_{T,P,N} \tag{24}$$

$$V(T, P, N) \equiv \nu^*_{T,P,N}\ . \tag{25}$$

It is important to keep in mind that $E(T, P, N)$ and $V(T, P, N)$ are deterministic functions, and not the fluctuating E and V.

Now suppose our system is very large. Then, because $G^L_{T,P,N}$ is extensive (scales with N), the summation (22) is well-approximated by a saddle point, as it is dominated by its most likely value:

$$Z(T, P, N) \underset{N\to\infty}{\approx} e^{-\beta G^L_{T,P,N}(E(T,P,N),\, V(T,P,N))} \tag{26}$$

$$\implies G^L_{T,P,N}(E(T, P, N),\, V(T, P, N)) \underset{N\to\infty}{\approx} -k_B T \ln Z(T, P, N) = G(T, P, N)\ . \tag{27}$$

The Landau-Gibbs free energy, evaluated at $E(T, P, N)$ and $V(T, P, N)$, is approximately equal to the Gibbs free energy $G(T, P, N)$ (Def. 2.3). Thus, we can say

$$G(T, P, N) \underset{N\to\infty}{\approx} E(T, P, N) + PV(T, P, N) - TS(E(T, P, N),\, V(T, P, N))\ . \tag{28}$$

2.4 Alternate derivation: canonical to isobaric

What if, instead, we had started with a system in the canonical ensemble (defined by variables T, V, N), and then considered a subsystem it in which the volume can vary? See, e.g., Fig. 3. This will also result in the same isobaric/isothermal ensemble, but the derivation is a bit different.

Start with a system in the canonical ensemble, which we will treat as the "total" with subscripts "tot". Suppose it has temperature T, fixed volume V_{tot}, a fixed number of particles N_{tot}, and states φ_{tot} with probability given by

$$P^{\text{tot}}_{T,V_{\text{tot}},N_{\text{tot}}}(\varphi_{\text{tot}}) = \frac{e^{-\beta E_{\text{tot}}(\varphi_{\text{tot}})}}{Z^{\text{tot}}(T, V_{\text{tot}}, N_{\text{tot}})}\ , \qquad Z^{\text{tot}}(T, V_{\text{tot}}, N_{\text{tot}}) = \sum_{\varphi_{\text{tot}}} e^{-\beta E_{\text{tot}}(\varphi_{\text{tot}})}\ . \tag{29}$$

Now consider a subsystem of this system, with fixed $N \ll N_{\text{tot}}$ particles, and with unconstrained volume V and states φ. We call the rest of the tot. system the reservoir, with N_r particles, volume $V_{\text{tot}} - V$, and states φ_r; i.e. $N_{\text{tot}} = N_r + N$,

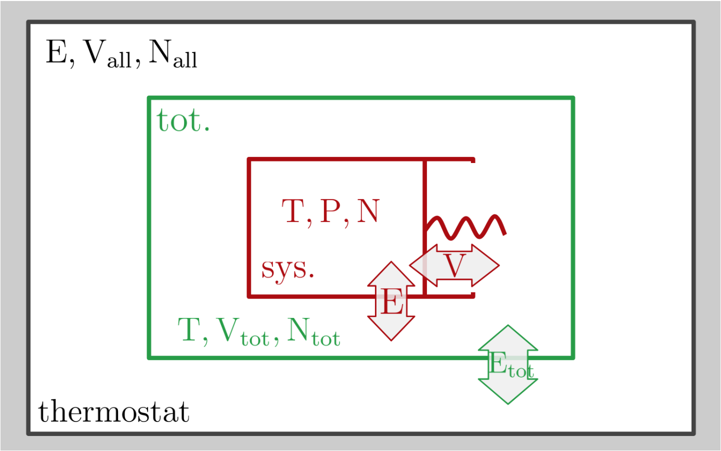

Figure 3: Moving from the microcanonical to the canonical to the isobaric/isothermal ensemble. The subsystem (sys.) has fluctuating energy E and volume V, and fixed particle number N. It exchanges energy and volume with its reservoir (tot.), which has fixed temperature T, volume V_{tot}, and particle number N_{tot}, and itself exchanges energy with a thermostat that has fixed energy E_{all}, volume V_{all}, and particle number N_{all}.

$V_{\text{tot}} = V_r + V$, and $\varphi_{\text{tot}} = \varphi \otimes \varphi_r$. Then the probability of the subsystem being in a state φ is

$$
\begin{aligned}
P^{\text{tot}}_{T,V_{\text{tot}},N_{\text{tot}}}(\varphi) &= \sum_{\varphi_r} \frac{e^{-\beta E_{\text{tot}}(\varphi\otimes\varphi_r)}}{Z_{\text{tot}}(T,V_{\text{tot}},N_{\text{tot}})} = \sum_{\varphi_r} \frac{e^{-\beta E_r(\varphi_r)-\beta E(\varphi)}}{Z_{\text{tot}}(T,V_{\text{tot}},N_{\text{tot}})} && (30)\\
&= e^{-\beta E(\varphi)} \sum_{\varphi_r} \frac{e^{-\beta E_r(\varphi_r)}}{Z_{\text{tot}}(T,V_{\text{tot}},N_{\text{tot}})} \equiv e^{-\beta E(\varphi)} \frac{Z_r(T,V_{\text{tot}}-V,N_r)}{Z^{\text{tot}}(T,V_{\text{tot}},N_{\text{tot}})} && (31)\\
&\equiv \frac{e^{-\beta E(\varphi)-\beta F_r(T,V_{\text{tot}}-V(\varphi),N_r)}}{Z_{\text{tot}}(T,V_{\text{tot}},N_{\text{tot}})} \approx \frac{e^{-\beta E(\varphi)-\beta V(\varphi)\frac{\partial F_r}{\partial V_{\text{tot}}}(T,V_{\text{tot}},N_r)} Z_r(T,V_{\text{tot}},N_r)}{Z_{\text{tot}}(T,V_{\text{tot}},N_{\text{tot}})} && (32)\\
&\equiv \frac{e^{-\beta E(\varphi)-\beta P V(\varphi)}}{Z} \,. && (33)
\end{aligned}
$$

Now, the pressure is defined as

$$P \equiv \frac{\partial F_r}{\partial V_{\text{tot}}}(T,V_{\text{tot}},N_r) \,. \tag{34}$$

The partition function, understood as a function of T, P, N, can be written as

$$Z(T,P,N) = \sum_{\varphi} e^{-\beta E(\varphi)-\beta P V(\varphi)} \,. \tag{35}$$

Note that this is equivalent to defining it as the Laplace transform of the *canonical* partition function,

$$
\begin{aligned}
Z(T,P,N) &= \int_0^\infty dV \sum_{\varphi,\, V(\varphi)=V} e^{-\beta E(\varphi)-\beta P V(\varphi)} = \int_0^\infty dV e^{-\beta P V} \sum_{\varphi,\, V(\varphi)=V} e^{-\beta E(\varphi)} && (36)\\
&= \int_0^\infty dV e^{-\beta P V} Z_{\text{cano.}}(T,V,N) \,. && (37)
\end{aligned}
$$

The probability of the macrostate V can then be written as

$$P_{T,P,N}(V) = \frac{e^{-\beta P V} Z_{\text{cano.}}(T,V,N)}{Z(T,P,N)} \tag{38}$$

3 Thermodynamics recap

When our system is very, very large, its relative deviations from its most likely energy $E(T,V,N)$ and volume $V(T,P,N)$ (Eq. (23)) are small.[1] Thus we can treat this most likely energy and volume as the true intrinsic energy E and volume V of the system, which are related to T, P, and N through the constraints:

$$E(T,P,N),\, V(T,P,N) \equiv \underset{E,V}{\operatorname{argmax}} \big[TS(E,V,N) - E - PV\big] \,. \tag{39}$$

This is where thermodynamics departs from statistical mechanics: we stop treating E and V as fluctuating variables, and replace them with their most probable values. The system now lives in a phase space parametrized by E, T, V, P, N, μ, and whatever else we would like to add. The system is restricted to the sub-manifold of phase space defined by constraints like Eq. (39). Then, an "ensemble" is just defined by which axes we treat as "independent" variables, and which we treat as "dependent".

We could've written Eq. (39) as a sequence of two Legendre transforms (micro → canonical → isobaric/isothermal):

$$\begin{aligned} V(T,P,N) &\equiv \underset{V}{\operatorname{argmax}} \big[-F(T,V,N) - PV\big] \equiv \underset{V}{\operatorname{argmax}} \big[TS(E(T,V,N),V,N) - PV - E(T,V,N)\big] \,, \quad \text{where} \qquad (40) \\ E(T,V,N) &\equiv \underset{E}{\operatorname{argmax}} \big[TS(E,V,N) - E\big] \,. \qquad (41) \end{aligned}$$

Note that, in thermodynamics, the Legendre and Laplace transforms play equivalent roles:

> **Remark 3.1: log(Laplace transform + Saddle point) = Legendre transform**
>
> Consider a function $\varphi(y)$ for $y \in \mathbb{R}$. Let's define another function $\psi(x)$ by
>
> $$e^{\psi(x)} \equiv \int_{-\infty}^{\infty} dy e^{xy-\varphi(y)} \,. \tag{42}$$
>
> Then we say that $e^{\psi(-x)}$ is the **Laplace transform** of $e^{-\varphi(y)}$. (This is how we convert the partition functions from one ensemble to another; see Eq. (36).)
>
> Now, let's suppose $xy - \varphi(y)$ is very large near its maximum (e.g. it is extensive, and $N \to \infty$). Then, a saddle point approximation of Eq. (42) gives us
>
> $$\psi(x) \approx \sup_y \big[xy - \varphi(y)\big] \,. \tag{43}$$
>
> But this simply states that $\psi(x)$ is the **Legendre transform** of $\varphi(y)$. This is how we relate potential functions (S, F, G, etc.) in thermodynamics.

Two ensembles which differ in only a single conjugate variable (e.g. (E,V,N) vs. (T,V,N)) are related by performing a Legendre transform on the unmatched variable.

Here are some examples of ensemble-to-ensemble conversions:

Micro → Cano	$F(T,V,N) = \inf_E \big[E - TS(E,V,N)\big]$,	$E(T,V,N) = \underset{E}{\operatorname{argmax}} \big[TS(E,V,N) - E\big]$,	$\frac{1}{T(E,V,N)} = \frac{\partial S}{\partial E}(E,V,N)$
Cano → Isobar/isoth	$G(T,V,N) = \inf_V \big[PV + F(T,V,N)\big]$,	$V(T,P,N) = \underset{V}{\operatorname{argmax}} \big[PV - F(T,V,N)\big]$,	$P(T,V,N) = \frac{\partial F}{\partial V}(T,V,N)$
Cano → Grand	$Q(T,V,\mu) = \inf_N \big[\mu N + F(T,V,N)\big]$,	$N(T,V,\mu) = \underset{N}{\operatorname{argmax}} \big[\mu N - F(T,V,N)\big]$,	$\mu(T,V,N) = \frac{\partial F}{\partial N}(T,V,N)$

Once you have fixed all parameters to have these relationships, *then* you can use relations like

$$F = E - TS \,, \quad G = PV - F \,, \quad Q = \mu N - F \,. \tag{44}$$

Note that the constraints are exclusively between conjugate variables and thermodynamic potentials. How do we relate non-conjugate variables? That's the role of **equations of state** like the ideal gas law $PV = Nk_BT$. Before statistical mechanics, they were empirical, but now we derive them. But either way, you need to invoke some physics to find them.

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[1] This can be rigorously stated as a consequence of the central limit theorem.