

§ 5 Basics of (statistical) Thermodynamics

We will consider a "simple" thermodynamic system:

- macroscopically homogeneous, unchanged, no external fields acting on it, "large enough"
- ↳ bucket of water

5.1 Four Postulates of Statistical Thermodynamics

- 1) Equilibrium states of simple thermodynamic systems are macroscopically uniquely defined by the inner energy (U), the volume (V) and the number of particles (N).
 - (U, V, N) are the extensive variables of the system.
 - a macroscopic state can be achieved by many compatible microstates
 - pressure (p), temperature (T) are examples of intensive variables
 - intensive variables are related to extensive ones
→ equations of state (ideal gas: $pV = Nk_B T$)
 $pV = nRT$

- 2) For every thermodynamic system there is a function of the extensive variables

$$S = S(U, V, N)$$

defined for all equilibrium states, called entropy.

Upon lifting of restrictions (start mixing of different systems), the extensive variables of the new equilibrium

adjust so that S becomes maximal.

- 3) S is extensive, continuous, totally differentiable, and monotonously increasing with U :

$$\frac{\partial S}{\partial U} \Big|_{V,N} \geq 0$$

This implies that the inverse $U(S,V,N)$ is always possible to find, and S being maximal is related to U being minimal.

- 4) For every system with

$$\frac{\partial U}{\partial S} \Big|_{V,N} = 0$$

the entropy disappears, i.e. $S \rightarrow 0$.

5.2 Equilibrium Processes and Equations of State

We start from the inner energy $U(S,V,N)$ and consider its total differential

$$dU = \underbrace{\frac{\partial U}{\partial S} \Big|_{V,N}}_T dS + \underbrace{\frac{\partial U}{\partial V} \Big|_{S,N}}_{-P} dV + \underbrace{\frac{\partial U}{\partial N} \Big|_{S,V}}_{\mu} dN$$

The above implies that $T = T(S,V,N)$, $P = P(S,V,N)$, and $\mu = \mu(S,V,N)$ are equations of state. Also:

$$\begin{aligned} T dS &= \delta Q && \text{Change of the thermal energy} \\ -P dV &= \delta W_{\text{mech}} && \text{Change of the mechanical energy} \\ \mu dN &= \delta W_{\text{chem}} && \text{Change of the chemical energy} \end{aligned}$$

5.3 Thermodynamic Potentials

$U(S, V, N)$ is a thermodynamic potential of only the extensive variables.

Intensive variables are related to extensive ones. This allows us to define "new" thermodynamic potentials that contain a mix of extensive and intensive variables.

$$\begin{array}{ccc} U(S, V, N) & \xrightarrow{\substack{\text{Legendre} \\ \text{transformation}}} & F(T, V, N) = U - TS \quad \text{free energy} \\ & & H(S, P, N) = U + PV \quad \text{enthalpy} \\ & & G(T, P, N) = U - TS + PV \\ & & \qquad \qquad \qquad \text{Gibbs free energy} \end{array}$$

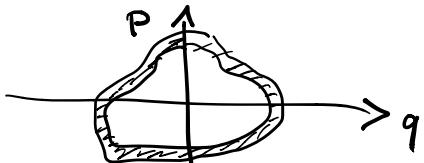
§ 6 Microcanonical Ensemble and Entropy

6.1 Probability density explicitly

Let's now proceed with finding an expression for the probability density $s(x)$. We do so with the help of a few reasonable arguments here to motivate the solution:

- system has fixed volume V , particle number N , and is described by Hamiltonian $H(x)$
- The energy of the system is in the interval

$$E < H(x) \leq E + \delta E$$



- There are a lot of phase space points \underline{x} within fixed energy interval. With the macroscopic variable E , we can have very many possible microscopic realizations of states $\underline{x}(t)$.
- Each of these points in phase space is equally likely. This property is ergodicity and it is not trivial to show.
- Each state that is compatible with (E, V, N) has the same probability.

Overall that means that

$$S(\underline{x}) = \begin{cases} C_E & \text{for } E < H(\underline{x}) \leq E + \delta E \\ 0 & \text{else} \end{cases}$$

The value of C_E do not depend on \underline{x} . We can determine its value from the normalization condition:

$$\int S(\underline{x}) d^{GN} \underline{x} = C_E \int_{E < H(\underline{x}) \leq E + \delta E} d^{GN} \underline{x} = C_E \omega(E) = 1$$

so $C_E = \frac{1}{\omega(E)}$, where $\omega(E)$ is the volume of the energy shell.

and

$$S(\underline{x}) = \begin{cases} \frac{1}{\omega(E)} & \text{for } E < H(\underline{x}) \leq E + \delta E \\ 0 & \text{else} \end{cases}$$

This is the microcanonical distribution and fulfills the stationary Liouville equation.

6.2 Entropy: Gibbs Functional

We realize from previous sections that all relevant observables can be determined as averages using $s(x, t)$.
In principle.

In practice, all arguments using Hamiltonian flows and phase space arguments (ergodicity) are rather cumbersome.

Can this be (largely) avoided when our main interest is more macroscopic?

Yes! The central quantity of statistical thermodynamics is entropy, which we have introduced via the few postulates.

↳ Gibbs Functional

$$S = -k_B \int s(x) \ln (c_s(x)) d^6x$$

We can turn this around: Extremizing S under certain conditions (normalization of probability density) defines the probability density uniquely.

6.3 Probability density via the Gibbs functional

Condition: $\int s(x) d^6x = 1$

\Rightarrow Maximize S under this constraint using the method of linear variations:

$$\delta \left\{ S + \lambda \left[\int s(x) d^6x - 1 \right] \right\} = 0$$

How to do that? We let $s \rightarrow s + \delta s$ and consider

$$\begin{aligned}
 & S(s + \delta s) + \lambda \left[\int (s + \delta s) d^{6N}x - 1 \right] - S(s) - \lambda \left[\int s d^{6N}x - 1 \right] \\
 &= S(s + \delta s) - S(s) + \lambda \int \delta s d^{6N}x \\
 &= -\hbar_B \int (s + \delta s) \ln(\zeta(s + \delta s)) d^{6N}x + \hbar_B \int s \ln(\zeta s) d^{6N}x \\
 &\quad + \lambda \int \delta s d^{6N}x
 \end{aligned}$$

To proceed, we evaluate:

$$\begin{aligned}
 \ln(\zeta(s + \delta s)) &= \ln(\zeta s \left(1 + \frac{\delta s}{s}\right)) \\
 &= \ln(\zeta s) + \underbrace{\ln\left(1 + \frac{\delta s}{s}\right)}_{\frac{\delta s}{s} - \frac{1}{2}\left(\frac{\delta s}{s}\right)^2 + \dots}
 \end{aligned}$$

linear variation

$$\begin{aligned}
 \dots &= -\hbar_B \int (s + \delta s) \left(\ln(\zeta s) + \frac{\delta s}{s} \right) d^{6N}x \\
 &\quad + \hbar_B \int s \ln(\zeta s) d^{6N}x + \lambda \int \delta s d^{6N}x
 \end{aligned}$$

only considering terms linear in δs

$$= -\hbar_B \int (\delta s + \delta s \ln(\zeta s)) d^{6N}x + \lambda \int \delta s d^{6N}x$$

$$= \underbrace{\{-\hbar_B - \hbar_B \ln(\zeta s) + \lambda\}}_{\text{red}} \delta s d^{6N}x \stackrel{!}{=} 0$$

This can only work if the term in $\{ \}$ vanishes:

$$-\frac{k_B}{\lambda} - \ln(\zeta) + \lambda = 0$$

$$\ln(\zeta) = \frac{\lambda}{k_B} - 1$$

$$\zeta(x) = \frac{1}{C} \exp\left(-\frac{\lambda}{k_B} - 1\right) = k$$

Energy is only in interval $E < H(x) \leq E + \delta E$

$$\zeta(x) = \begin{cases} k & \text{for } E \leq H(x) \leq E + \delta E \\ 0 & \text{else} \end{cases}$$

With the same argument as before

$$\int \zeta(x) d^{3N}x = k \cdot w(E) = 1$$

We can also calculate the entropy:

$$S = -k_B \int_{E < H(x) \leq E + \delta E} \frac{1}{w(E)} \ln\left(\frac{C}{w(E)}\right) d^{3N}x = -k_B \ln\left(\frac{C}{w(E)}\right).$$

$$C = N! h^{3N} \quad h: \text{Planck's constant}$$

$$S(E, V, N) = k_B \ln\left(\frac{w(E, V, N)}{N! h^{3N}}\right)$$