

Statistical Mechanics 3/4H

typed up by B. S. H. Mithrandir

- *Last compiled: August 2021*
- Adapted from notes of Veronika Hubeny and someone else (maybe Mukund?), Durham
- This was part of the Durham 3/4H elective. Includes introduction to classical thermodynamics and some quantum systems.
- It is sometimes said that there are probably two ways to approach thermodynamics: start from classical thermodynamics first, or start from a stat mech approach. These notes take the latter approach. From a physical understanding point of view, these particular notes might be more informative / useful if the intended user already has some exposure already to the traditional way of approaching thermodynamics.
- **TODO!** diagrams
- **TODO!** probably wants more context...
- **TODO!** to possibly merge in some other notes (e.g. expand a bit more on classical thermodynamics; or maybe not and keep it separate to highlight differences in approach)

Licensed under the Apache License, Version 2.0 (the “License”); you may not use this file except in compliance with the License. You may obtain a copy of the License at <http://www.apache.org/licenses/LICENSE-2.0>. Unless required by applicable law or agreed to in writing, software distributed under the License is distributed on an “AS IS” BASIS, WITHOUT WARRANTIES OR CONDITIONS OF ANY KIND, either express or implied. See the License for the specific language governing permissions and limitations under the License.

The aim is to describe thermodynamics in **equilibrium**.

1.0.1 Postulates and definitions

Extensive variables X_i of a thermodynamic system are those that depend and scales proportionally to the system size. The set of all extensive variables are sufficient to describe the system in equilibrium. Examples include

- energy
- volume
- charge
- number of particles

Thermodynamic system can either be **isolated** or **interacting** with an external environment. Isolated systems do not exchange any of the extensive parameters with the environment.

Thermodynamic postulate 1:

There exists an equilibrium state.

Proposition 1.0.1 (Generalised first law of thermodynamics) *At equilibrium,*

$$\frac{dX_i}{dt} = 0 \quad (1.1)$$

for all extensive variables X_i in a system.

The above is usually phrased as¹

$$\delta U = \delta Q + \delta W, \quad (1.2)$$

where U is the **internal energy**, Q is the **heat**, and W is **work done**. The conservation of internal energy gives

$$dU = T dS - P dV + \phi_i q_i, \quad (1.3)$$

¹ Sign of W depends on convention. Positive sign here as energy transferring into system.

where S is the **entropy** (see later), T is temperature, P is **pressure**, V is **volume**, and ϕ_i and q_i denote some other form of change. The exact definitions of some of these variables with respect to the more familiar thermodynamic quantities will be provided later.

Thermodynamic postulate 2:

*There exists a function S called the **entropy** for all thermodynamic systems such that*

1. $S = S(X)$, $X = \{X_i\}$, and S is itself extensive;
2. $S \in C^\infty$ (usually)
3. S is maximised as a function of X when the system is in thermal equilibrium.

The two postulates constrain the allowed physical processes that go on within a thermodynamic system.

Example Given two systems $S^{1,2}$ with extensive parameters $X^{1,2}$ respectively, for $\mathcal{S} = S^1 \cup S^2$, the total set of extensive parameters is $X = X^1 + X^2$. Since entropy is maximised, $S(X) = S(X^1 + X^2) \geq S_1(X^1) + S_2(X^2)$.

Suppose $S(X) = S_1(X^1 + \delta X^1) + S_2(X^2 + \delta X^2)$, where δX^2 is the required change to bring the system total system to equilibrium. Then we want $\delta X^1 + \delta X^2 = 0$. Considering the variation, we have

$$\delta S = \frac{\partial S_1}{\partial X^1} \delta X^1 + \frac{\partial S_2}{\partial X^2} \delta X^2 = \delta X^1 \left(\frac{\partial S_1}{\partial X^1} - \frac{\partial S_2}{\partial X^2} \right).$$

Since $\delta S \geq 0$, the sign of δX^1 is the same as $(\partial S_1 / \partial X^1 - \partial S_2 / \partial X^2)$, thus determining the direction of flow for X .

Some properties of entropy:

- $S(X)$ is a homogeneous function of degree 1, i.e. $S(\alpha X) = \alpha S(X)$ for some scalar α ;
- the defining relation of entropy in terms of other extensive parameters is called the **entropy fundamental relation**, which provides a complete specific formulation of the thermodynamic system;
- physically, the entropy measures the amount of disorder in the system.

Intensive parameters Z_i are those that are **conjugate** to the extensive parameters X_i , i.e.

$$Z_i = \frac{\partial S}{\partial X_i}. \quad (1.4)$$

Superscripts denote system, subscripts denote variable within a system.

Clearly Z_i has to be homogeneous functions of degree 0, and $Z_i(X)$ is called the **equation of state**, but requires additional information in order to have a complete specification of the thermodynamic system.

Lemma 1.0.2 *If two systems $\mathcal{S}^{1,2}$ interact and exchange extensive variables $X^{1,2}$, at equilibrium, we have $Z^1 = Z^2$.*

Proof Since we are at equilibrium, we aim to maximise $S = S^1 + S^2$ keeping $X = X^1 + X^2$ fixed. This can be done either by variation, with

$$0 = \delta S = \delta X^1 \left(\frac{\partial S_1}{\partial X^1} - \frac{\partial S_2}{\partial X^2} \right) = (Z^1 - Z^2) \delta X^1 \quad \Rightarrow \quad Z^1 = Z^2,$$

or by the method of Lagrange multipliers, we aim to maximise $S - \lambda(X^1 + X^2)$ to get

$$\frac{\partial S}{\partial X^1} - \lambda = 0, \quad \frac{\partial S}{\partial X^2} - \lambda = 0$$

which implies $\lambda = Z^1 = Z^2$. ■

Zerth law of thermodynamics²:

For two systems in thermal equilibrium with each other, $Z_i^1 = Z_i^2$ for all i .

When two systems $\mathcal{S}^{1,2}$ are not in equilibrium and $Z^1 > Z^2$, $dS > 0$ implies X flows from \mathcal{S}^1 to \mathcal{S}^2 , and we have a **directed flow**.

Instead of entropy S , we can take the internal energy U as the fundamental variable³. We have the **energetic fundamental relations** with intensive parameters

$$Y_i = \frac{\partial U}{\partial X_i}. \quad (1.5)$$

From this, we note that

- **temperature** T is conjugate to entropy S , i.e.

$$T = \frac{\partial U}{\partial S}; \quad (1.6)$$

- **pressure** P is conjugate to volume V , i.e.

$$P = -\frac{\partial U}{\partial V}; \quad (1.7)$$

- **chemical potential** μ is conjugate to particle number N , i.e.

$$\mu = \frac{\partial U}{\partial N}. \quad (1.8)$$

² More commonly, if two systems are in thermal equilibrium with a third system, then they are in equilibrium with each other. This is a statement about *transitivity* and establishes thermal equilibrium as an equivalence relation from a mathematical point of view.

³ And really is what would be the more traditional way of introducing classical thermodynamics.

All signs are by convention. Occasionally, we employ the **inverse temperature**⁴ variable β given by

$$\beta = \frac{1}{T} = \frac{\partial S}{\partial U}. \quad (1.9)$$

⁴ Sometimes this is defined with a factor of the Boltzmann constant k_B , i.e. $\beta = (k_B T)^{-1}$.

Example An alternative phrasing of the first law of thermodynamics⁵ is given as energy conservation (Einstein summation convention implied)

$$dU = T dS + \frac{\partial U}{\partial X_i} dX_i = T dS + Y_i dX_i. \quad (1.10)$$

⁵ Actually the more traditional way of stating the first law.

Then, by rephrasing in the conjugate variables, we have

$$\begin{aligned} dS &= \beta dU + Z_i dX_i \\ &= \beta(T dS + Y_i dX_i) + Z_i dX_i \\ &= dS + (\beta Y_i + Z_i) dX_i, \end{aligned}$$

implying

$$Y_i = -TZ_i, \quad (1.11)$$

i.e. all individual intensive parameters associated with T and S are related by a factor of temperature.

A system is said to undergo a **quasi-static** process if, at every instant of time along the path in the phase space, one can approximate the system as being in equilibrium. A quasi-static process is **adiabatic** if the system does not exchange heat with its surroundings, i.e. $dS = 0$ along the appropriate curve in phase space.

1.0.2 Some examples

1. Consider an **ideal gas**⁶ in equilibrium, which is made to undergo a quasi-static expansion from V_i to V_f adiabatically. During this process, $PV^\gamma = \text{constant}$, where γ is some number (the **adiabatic index** or the **heat capacity ratio**). We aim to calculate the change in internal energy of the gas, and the work done and heat absorbed by the gas when it goes from (P_i, V_i) to (P_f, V_f) .

⁶ Randomly moving point particles that are not subject to inter-particle interactions.

Starting from the first law with $dU = T dS - P dV$, since the process is adiabatic, $dS = 0$, so $dU = -P dV$. By assumption,

$$PV^\gamma = P_i V_i^\gamma = C \quad \Rightarrow \quad P = \frac{P_i V_i^\gamma}{V^\gamma},$$

so integrating gives

$$\begin{aligned}\Delta U &= U_f - U_i = \int_{V_i}^{V_f} -\frac{P_i V_i^\gamma}{V^\gamma} dV \\ &= -P_i V_i^\gamma \left[\frac{V^{-\gamma+1}}{-\gamma+1} \right]_{V_i}^{V_f} \\ &= \frac{P_f V_f - P_i V_i}{\gamma - 1}\end{aligned}$$

via using $P_i V_i^\gamma = P_f V_f^\gamma$.

2. From $S \sim (UVN)^{1/3}$, derive the equation of state.

This is asking for the intensive variables and their relations to the extensive variables. For some constant c , we have $U = cS^3/(VN)$, so

$$T = \frac{\partial U}{\partial S} = \frac{3cS^2}{VN}, \quad P = -\frac{\partial U}{\partial V} = \frac{cS^3}{V^2N}, \quad \mu = \frac{\partial U}{\partial N} = -\frac{cS^3}{VN^2}.$$

3. Derive the **Euler relation**

$$U(S, X_i) = TS + X_i Y_i, \quad (1.12)$$

where Y_i are the intensive variables associated with X_i via the internal energy (instead of a entropy).

Since U is extensive, we have $U(\lambda S, \lambda X_i) = \lambda U(S, X_i)$ by homogeneity, so by chain rule and taking a derivative with respect to λ ,

$$\frac{\partial U}{\partial(\lambda S)}(\lambda S, \lambda X_i) \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda X_i)}(\lambda S, \lambda X_i) \frac{\partial(\lambda X_i)}{\partial \lambda} = U(S, X_i).$$

If we set $\lambda = 1$, then the result follows on noting $\partial U/\partial S = T$, and $\partial U/\partial X_i = Y_i$.

4. Prove the **Gibbs–Duhem relation**

$$S dT + X_i dY_i = 0. \quad (1.13)$$

Differentiating the Euler relation leads to

$$dU = T dS + S dT + X_i dY_i + Y_i dX_i,$$

and since the first law tells us $dU = T dS + Y_i dX_i$, the result follows.

5. Show that the Euler and Gibbs–Duhem relations can be written as

$$S = \frac{1}{T} U + Z_i X_i, \quad U d\left(\frac{1}{T}\right) + X_i dZ_i = 0,$$

where Z_i is the intensive variables associated with the entropy.

Recall that $Y_i = -TZ_i$ and $dU = T dS + Y_i dX_i$, which implies the first relation via substitution and integration. Differentiating the first relation leads to

$$dS = U d\left(\frac{1}{T}\right) + \frac{1}{T} dU + X_i dZ_i + Z_i dZ_i,$$

and upon using the first law by substituting dS leads to the second relation.

6. For an ideal gas, given $PV = nRT$ and $U = (3/2)RNT$, where R is the universal gas constant, derive the associated **entropic fundamental relation** $S(U, V, N)$.

To make the equation more exact, consider scaling by N as $u = U/N$, $v = V/N$, which leads to

$$Pv = RT, \quad u = \frac{3}{2}RT.$$

Note that we have

- X_i : V, N ;
- Y_i : $-P, \mu$,
- Z_i : $P/T, -\mu/T$.

Using the Gibbs–Duhem relation and scaling by N leads to

$$u d\left(\frac{1}{T}\right) + v d\left(\frac{P}{T}\right) = d\left(\frac{\mu}{T}\right).$$

By computing the relevant derivatives, we have

$$d\left(\frac{\mu}{T}\right) = -\frac{3R}{2} \frac{du}{u} - R \frac{dv}{v},$$

which upon integrating leads to

$$\frac{\mu}{T} = \frac{3R}{2} \log \frac{u}{u_0} - R \log \frac{v}{v_0}.$$

Using Euler's relation in the form

$$S = \frac{1}{T}U + \frac{P}{T}V - \frac{\mu}{T}N,$$

substituting accordingly results in

$$S(U, V, N) = \frac{5}{2}NR + NR \log \left(\frac{u^{3/2}v}{u_0^{3/2}v_0} \right).$$

1.0.3 *Thermodynamic potentials*

Recall that the Legendre transform of a given function $f(x, y)$ is achieved via the consideration of

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy \equiv u(x, y) dx + v(x, y) dy.$$

To define f as a function of u rather than x , consider

$$g(v, y) = f - ux,$$

which then implies

$$dy = df - u dx - x du = v dy - x du,$$

where $v = \partial g / \partial y$ and $x = \partial g / \partial u$.

The Legendre transform is an involute transformation of real valued convex functions in one dimension, such that their derivatives of the original and transformed functions are inverses of each other. Physically is used to convert functions of one quantity to a function of its conjugate variable (e.g. position to momenta, pressure to volume, temperature to entropy, and vice-versa). The **thermodynamic potentials** are Legendre transforms of U with respect to the various extensive parameters. Some important ones are:

- **Helmholtz free energy**, which is the transformation of U with respect to S , given by

$$F(T, X_i) = U - TS. \quad (1.14)$$

- **Enthalpy**, which is the transformation of U with respect to V , given by

$$H(P, S, X_i) = U + PV. \quad (1.15)$$

- **Gibbs free energy**, which is the transformation of U with respect to S and V , given by

$$G(T, P, X_i) = U - TS + PV. \quad (1.16)$$

Sometimes it is easier to consider these potentials instead of directly trying to find the measurements for the extensive parameters. Which one we choose depends on how the system is described. For example, if it is natural to vary T for example, then we consider F .

Example Show that $dF = -S dT + Y_i dX_i$.

From the definition of the Helmholtz free energy,

$$\begin{aligned} dF &= dU - T dS - S dT \\ &= (T dS + Y_i dX_i) - T dS - S dT \\ &= -S dT + Y_i dX_i. \end{aligned}$$

These could be thought of as the capacity to do mechanical and non-mechanical work (F), to do non-mechanical work and release heat (H), capacity to do non-mechanical (reversible) work (G), and capacity to do work and release heat U .

Since $dF = (\partial F/\partial T) dT + (\partial F/\partial X_i) dX_i$, we note that

$$-S(T, X_i) = \frac{\partial F}{\partial T}, \quad Y_i(T, X_i) = \frac{\partial F}{\partial X_i}, \quad (1.17)$$

and similar identities hold for the other thermodynamic potentials, i.e., from the thermodynamic potentials you can derive essentially all the things you want to know.

From the thermodynamic potentials, one can derive the **Maxwell relations**, which essentially relate the second derivatives of the potentials. For simplicity, we concentrate on a system with extensive parameters U, S, V and N . Recall that $dU = T dS - P dV + \mu dN$, so that

$$T = \left. \frac{\partial U}{\partial S} \right|_{V,N}, \quad P = - \left. \frac{\partial U}{\partial V} \right|_{S,N}, \quad \mu = \left. \frac{\partial U}{\partial N} \right|_{S,V}.$$

Assuming we have the relevant conditions required for partial derivatives to commute, then we would have for example

$$\left. \frac{\partial T}{\partial V} \right|_N = \frac{\partial}{\partial V} \left. \frac{\partial U}{\partial S} \right|_N = \frac{\partial}{\partial S} \left. \frac{\partial U}{\partial V} \right|_N = - \left. \frac{\partial P}{\partial S} \right|_N,$$

and many others. These can also be derived from F, H and G via

$$dF = -S dT - P dV + \mu dN,$$

$$dH = +T dS + V dP + \mu dN,$$

$$dG = -S dT + V dP + \mu dN.$$

In general, Maxwell relatives are reflective of the symmetry properties of the physical quantities. We have

$$\frac{\partial Y_i}{\partial X_j} = \frac{\partial X_i}{\partial Y_j}, \quad \frac{\partial Y_i}{\partial Y_j} = - \frac{\partial X_j}{\partial X_i}. \quad (1.18)$$

Some useful physical quantities arising from the thermodynamic potentials are as follows:

- **Specific heat**, defined as

$$c = T \frac{\partial S}{\partial T}. \quad (1.19)$$

For the specific heats we need to specify which quantities are being held fix. For example, if have hold volume fixed ($dV = 0$), then

$$c_V = T \left. \frac{\partial S}{\partial T} \right|_V = -T \left. \frac{\partial^2 F}{\partial T^2} \right|_V. \quad (1.20)$$

On the other hand, if we hold pressure fixed ($dP = 0$), then we have

$$c_P = T \left. \frac{\partial S}{\partial T} \right|_P = -T \left. \frac{\partial^2 G}{\partial T^2} \right|_P, \quad (1.21)$$

and note the appearance of the Gibbs instead of Helmholtz free energy appearing here. Note also that $\gamma = c_P/c_V$.

- The **susceptibility** (variation of extensive quantity with the corresponding intensive quantity) is defined as

$$\chi = \frac{\partial X}{\partial Y}, \quad (1.22)$$

for conjugate X and Y .

- The **compressibility** is defined as

$$\kappa = -\frac{1}{V} \frac{\partial V}{\partial P}. \quad (1.23)$$

- The **coefficient of thermal expansion** is defined as

$$\alpha = \frac{1}{V} \frac{\partial V}{\partial T}. \quad (1.24)$$

2 Ensembles

An **(statistical) ensemble** considers a collection of a large (possibly infinite) number of virtual copies all at once, each of which represents a possible state that the real system might be in, and we consider obtaining the statistics of the ensemble¹. An ensemble can be thought of as a probability distribution for the state of the system.

¹ Concept introduced by Gibbs.

2.0.1 Recap on probability

Recall that, for a random variable X , the m^{th} **moment of probability** is defined as

$$\overline{X^m} = \langle X^m \rangle = \begin{cases} \sum_{i=1}^n x_i^m p(x_i), & X \text{ discrete} \\ \int x^m p(x) dx, & X \text{ continuous,} \end{cases} \quad (2.1)$$

where p are the relevant probability density functions (pdfs). For example, the usual mean (expectation) and variance are the first and second central moments respectively, i.e.

$$\mathbb{E}(X) = \mu = \langle X \rangle, \quad \text{Var}(X) = \sigma^2 = \langle (X - \mathbb{E}(X))^2 \rangle = \langle X^2 \rangle - \langle X \rangle^2.$$

The **moment generating function** is then defined as

$$M(t) = \int e^{xt} p(x) dx = \sum_{n=0}^{\infty} \frac{t^n}{n!} \langle x^n \rangle. \quad (2.2)$$

The moments are then computed by evaluating derivatives of $M(t)$ at $t = 0$ accordingly, i.e. $\langle x^n \rangle = M^{(n)}(0)$.

A **Bernoulli random variable** X is one that can only take two different values, and thus follow the **binomial distribution**

$$X \sim B(n, p_0), \quad P(X = k) = \binom{n}{k} p_0^k (1 - p_0)^{n-k}, \quad (2.3)$$

for some specified p_0 . The binomial distribution can be viewed as a Bernoulli trial repeated n times. The binomial distribution has some special limits:

- for $n \gg 1$ and $p_0 \ll 1$ such that $np_0 = \lambda < \infty$, we tend to the **Poisson distribution**

$$\frac{\lambda^k e^{-\lambda}}{k!} = P(X = k), \quad X \sim \text{Po}(\lambda). \quad (2.4)$$

- for $n \gg 1$, by the **central limit theorem**, we tend to the **Gaussian distribution**

$$\frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\mu)^2/(2\sigma^2)} = p(x), \quad X \sim N(\mu, \sigma). \quad (2.5)$$

Theorem 2.0.1 (Central limit theorem) Let $\{X_k\}$ be a sequence of mutually independent, identically distributed random variable whose mean and variance are defined as $\mu = \langle X \rangle$ and $\sigma^2 = \langle (X - \mu)^2 \rangle$. If $S_n = \sum X_k$ then, for all $x \in \mathbb{R}$,

$$\lim_{n \rightarrow \infty} P\left(\frac{S_n - n\mu}{\sqrt{n\sigma^2}} < x\right) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^x e^{-u^2/2} du,$$

where u is a re-scaled variable. □

Example (1d random walk) At every point on \mathbb{Z} , one can move left with probability $p_L = p$ and to the right with $p_R = 1 - p_L$. Starting from $x = 0$, the probability of finding the object at $x = m \in \mathbb{Z}$ after N steps is given by a binomial distribution. Suppose we move n_L steps left and a n_R steps right, then we have $n_L + n_R = N$ and $m = n_R - n_L$. Thus the probability of object being at $x = m$ after N steps is given by

$$P(X = m) = \binom{N}{n_R} p_R^{n_R} p_L^{n_L} = \binom{N}{(N+m)/2} p^{(N-m)/2} (1-p)^{(N+m)/2}.$$

It is clear that if $p = 1/2$, then $\langle X_N \rangle = 0$, otherwise there is a bias towards one direction.

2.0.2 Recap on classical mechanics

For a given **macrostate** (N, V, E) , at any given time t , is equally likely to be in any one of an extremely large number of distinct **microstates**, specified by the instantaneous position and momenta of all particles that constitute the system. As time passes, a system evolves through distinct microstates, and we aim to obtain the long time behaviour via averaging the microstates. One possible way is to consider an ensemble of copies characterised by the same macrostate, but ranging over microstates. Assuming ergodicity, time averaging corresponds to ensemble averaging, and we can decide to take one or the other depending on which is more convenient.

Recall that, given a Lagrangian $L(q, \dot{q}; t)$, where q is a generalised co-ordinate and dot denotes a partial time derivative, the Euler–Lagrange equations are given by

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0, \quad (2.6)$$

which is a set of n second order ODEs that determines all $q_i(t)$ given $2n$ initial conditions. By defining the conjugate momenta variable as $p_i = \partial L / \partial \dot{q}_i$, we consider the Legendre transform of the Lagrangian

$$H(q, p; t) = \sum_i \dot{q}_i p_i - L(q, \dot{q}; t),$$

where H is the Hamiltonian, which can be interpreted as the total energy in a system. The Hamilton–Jacobi equations are then

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad (2.7)$$

and now we have instead $2n$ first order ODEs. Time evolution of the system is then defined by the trajectory in the (q, p) phase space.

In general, we want to consider many particles in d dimensions interacting in a complicated fashion. We will generally be interested in the behaviour of the system in some narrow range of energies $H(p, q) \in (E - \delta E, E + \delta E)$. An ensemble will then be represented by a “swarm” of representative points moving on the phase space. We define a **density function** $\rho(p, q; t)$ as a measure of how the members of the ensemble are distributed over all possible microstates at different instances of time. For infinitesimal volume $d\omega$, $\rho d\omega$ gives the number of representative points around some specified (p, q) . We this, we define the **ensemble average** of a function $f(p, q)$ as

$$\langle f \rangle = \frac{\int f(p, q) \rho(p, q; t) d\omega}{\int \rho(p, q; t) d\omega}. \quad (2.8)$$

The ensemble is said to be **stationary** if ρ is time independent. This describes a system in equilibrium.

Theorem 2.0.2 (Liouville’s theorem) *The local density of points in the phase space ρ , as seen by a co-moving observe along the point’s trajectory, stays constant in time, i.e.*

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \{q, H\} = 0,$$

where $\{\cdot, \cdot\}$ is the Poisson bracket. □

Following from Liouville’s theorem, if a system is in equilibrium, $\partial \rho / \partial t = 0$, so that

$$\{q, H\} = \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i = 0,$$

which greatly reduces the arbitrary nature of ρ .

2.1 Microcanonical ensemble

Mathematically, we assume the density function $\rho(q, p; t)$ is constant in the accessible regions of the phase space. Physically, we assume we have a completely isolated system with some Hamiltonian H . We want to fix the total energy to be E_0 , and allow for some fluctuations of size δE around E_0 . Since the density function $\rho(p, q; t)$ gives the probability of finding the representative points at (q, p) in the ensemble, the **microcanonical ensemble** Σ_M corresponds to having equal probability of finding any specific microstate in the energy range $(E_0 \pm \delta E)$.

Example For $\delta E = 0$, we constrain the available region of phase space to the hyperspace $H = E_0$, i.e. $\rho(q, p; t) \propto \delta(H(q, p) - E_0)$.

In general, we define

$$\Omega(E_0, \delta E) = \sum_n \int_{E_0 - \delta E}^{E_0 + \delta E} \delta(E_n - E) dE, \quad (2.9)$$

which is the number of microstates in the energy band $(E_0 \pm \delta E)$. Here, E_n is the energy of the n microstate, and equal probabilities imply that the probability of finding a state with energy E_n is

$$p_n = \int_{E_0 - \delta E}^{E_0 + \delta E} \frac{\delta(E_n - E)}{\Omega(E_0, \delta E)} dE.$$

Note that Σ_M is assumed to be a stationary ensemble, so the ensemble average must be time-independent. Let \bar{f} denote the ensemble average of f , and $\langle f \rangle_t$ denote the time average of f , then

$$\bar{f} = \langle \bar{f} \rangle_t = \overline{\langle f \rangle_t} = \langle f \rangle_t,$$

and this is the long time average of f and corresponds to the value one would obtain on making an appropriate measurement of f .

Knowledge of the number of microstates of the system enables us to define the entropy using the **Boltzmann formula**

$$S = k_B \log \Omega, \quad (2.10)$$

where k_B is the **Boltzmann constant**². To motivate this formula, consider two systems $\mathcal{S}_{1,2}$, each of which is separately in equilibrium with energies $E_{1,2}$ and number of microstates as $\Omega_1(E_1)$ and $\Omega_2(E_2)$. Bringing the two systems together and letting them equilibrate, the total energy $E = E_1 + E_2$ stays constant and the number of total microstates for the combined system is

$$\Omega(E_1, E_2) = \Omega_1(E_1)\Omega_2(E_2) = \Omega_1(E_1)\Omega_2(E - E_2) \equiv \Omega(E, E_1).$$

² $k_B = 1.380649 \times 10^{-23} \text{ J K}^{-1}$

We postulate that the energy distribution between the system occurs in such a way so as to maximise the total number of microstates of the combined system. Suppose equilibrium values of the energies are labelled as $E_{1,\text{eq}}$ and $E_{2,\text{eq}}$, then, by chain rule and definition of E_2 ,

$$\begin{aligned} 0 = \left. \frac{\partial \Omega}{\partial E_1} \right|_{E_{1,\text{eq}}} &= \left[\frac{\partial \Omega_1}{\partial E_1} \Omega_2(E_2) \right]_{E_{1,\text{eq}}} + \left[\frac{\partial \Omega_2}{\partial E_2} \Omega_1(E_1) \frac{\partial E_2}{\partial E_1} \right]_{E_{2,\text{eq}}} \\ &= \left[\frac{\partial \Omega_1}{\partial E_1} \Omega_2(E_2) \right]_{E_{1,\text{eq}}} - \left[\frac{\partial \Omega_2}{\partial E_2} \Omega_1(E_1) \right]_{E_{2,\text{eq}}}, \end{aligned}$$

and since $\Omega_{1,2} \neq 0$, this implies

$$\left. \frac{\partial \Omega_1}{\partial E_1} \right|_{E_{1,\text{eq}}} = \left. \frac{\partial \Omega_2}{\partial E_2} \right|_{E_{2,\text{eq}}}.$$

This means that the condition of equilibrium boils down to the quantity

$$\beta \equiv \frac{\partial \Omega}{\partial E}, \quad (2.11)$$

which is to be constant throughout the system. It is natural to associate β with $(k_B T)^{-1}$, since

$$\left. \frac{\partial S}{\partial E} \right|_{V,N} = \frac{1}{T} = k_B \beta.$$

Let the total number of states accessible to a system with energy less than or equal to E be

$$\Sigma(E) = \int_0^E \Omega(E') \, dE',$$

and let the **density of states** be

$$D(E) = \frac{d\Sigma(E)}{dE}. \quad (2.12)$$

Example For an ideal gas, consider N free gas particles of mass m in a volume V with total energy E . To calculate the entropy of this system, note that the canonical Hamiltonian for this system is

$$H = \sum_{i=1}^N \frac{|p_i|^2}{2m},$$

implying

$$\Sigma(E) = \int_{H \leq E} \frac{d\omega}{\omega_0},$$

where ω_0 is the volume occupied by a single microstate³. We need to convert the integral over volume in phase space to be specified in terms of E . For this, note that

$$d\omega = \prod_{i=1}^{3N} dq_i \, dp_i = V^N \prod_{i=1}^{3N} dp_i,$$

³ It turns out $\omega_0 = h^{3N}$ in 3-space, where h is the Planck's constant.

so that

$$\Sigma(E) = \frac{V^N}{\omega_0} \int_R \prod_{i=1}^{3N} dp_i = \frac{V^N}{\omega_0} \text{vol} \left(S_r^{3N-1} \right),$$

where $R = \{p_i | \sum_{i=1}^N |p_i|^2 \leq 2mE\}$, and S_r^{3N-1} is the $(3N-1)$ -sphere of radius r . Now, it can be shown that the $(n-1)$ -sphere of unit radius has area

$$\text{area} \left(S_1^{n-1} \right) = \frac{2\pi^{n/2}}{\Gamma(n/2)}$$

where Γ is the gamma-function. So then

$$\begin{aligned} \text{vol} \left(S_r^{3N-1} \right) &= \int_0^r \text{area} \left(S_\rho^{n-1} \right) d\rho = \text{area} \left(S_1^{n-1} \right) \int_0^r \rho^{n-1} d\rho \\ &= \frac{2\pi^{n/2}}{\Gamma(n/2)} \frac{r^n}{n}, \end{aligned}$$

from which it follows that, taking $r = (2mE)^{1/2}$ (because R is a sphere of radius $(2mE)^{1/2}$)

$$\Sigma(E) = \frac{V^N}{h^{3N}} \frac{\pi^{3N/2}}{\Gamma(3N/2)} \frac{(2mE)^{3N/2}}{3N/2}.$$

For some small δ shell, we have the following relation between $\Sigma(N, V, E)$ and $\Omega(N, V, E, \delta)$:

$$\Omega \approx \frac{\partial \Sigma}{\partial E} \delta \approx \frac{3N}{2} \frac{\delta}{E} \Sigma$$

arguing that $3N \approx 3N-1$ for $N \gg 1$. So we have

$$\log \Omega \approx \log \Sigma + \log \frac{3N}{2} + \log \frac{\delta}{E}.$$

For $N \gg 1$ the last term can be dropped but the ordering between the first and second term is not obvious. However, using **Sterling's formula** where

$$\log N! \approx N \log N - N \quad \text{for} \quad N \gg 1, \quad (2.13)$$

noting that $\Gamma(N) \sim N!$, we have that

$$\begin{aligned} \log \Sigma &\approx N \left[\log \left(\frac{2m\pi EV^{2/3}}{h^2} \right)^{3/2} - \frac{3}{2} \log \frac{3N}{2} + \frac{3}{2} + O \left(\frac{\log N}{N} \right) \right] \\ &= O(N \log N), \end{aligned}$$

so we have $\log \Omega \sim \log \Sigma$ for $N \gg 1$. After tidying up factors, we obtain

$$S \approx k_B \log \Sigma \approx k_B N \left\{ \frac{3}{2} + \log \left[\left(\frac{4\pi mE}{3h^2 N} \right)^{3/2} V \right] \right\}.$$

Note normally there should be a $1/N!$ factor in the normalisation to account for the fact that particles are indistinguishable, which would then modify the resulting formula for the entropy given here to have the order one constant going from $3/2$ to $5/2$, and V replaced by V/N , resulting in the **Sackur-Tetrode equation**. As given here without the factor of $1/N!$, S is not extensive nor is it additive, resulting in **Gibbs' paradox**.

Compare the derived result here with one obtained from thermodynamics, where

$$S \sim S_0 + Nk_B \log \left(\frac{u^{3/2}v}{u_0^{3/2}v_0} \right).$$

One can derive the usual thermodynamic equations from S , for example,

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{V,N} = Nk_B \frac{3}{2} \frac{1}{E} \Rightarrow E = \frac{3Nk_B}{2} T,$$

which agrees with the $u = (3/2)RT$ relation we know from thermodynamics.

2.2 Canonical ensemble

Physically, it is easier to fix a system's temperature rather than the energy, as is the case for the microcanonical ensemble. Fixing a system's temperature can be achieved by coupling the system to a heat bath or reservoir. The corresponding ensemble is called the **canonical ensemble**, denoted \mathcal{E}_c . In this system, the energy can fluctuate between zero and plus infinity, and we can only meaningfully take about the probability p_r of finding a state of energy E_r . To determine p_r , we can either

1. regard the system as being in equilibrium with the reservoir at some common temperature T , and study the statistics of energy exchange, or
2. regard the system as a member of an ensemble \mathcal{E}_c at temperature T , and study the statistics of how the total energy E is shared between members of \mathcal{E}_c .

Taking the first approach, we consider a system S begin in equilibrium with a reservoir R at some temperature T . We want to find the most likely distribution of energy E_S of a system and E_R of the reservoir. For isolated $S \cup R$, the total energy $E = E_S + E_R$ is fixed, and we consider

$$\frac{E_S}{E} = 1 - \frac{E_R}{E} \ll 1.$$

For a given state of S , R will be in any of the states accessible to it, and we denote the number of such states $\Omega_R(E_R)$. At equilibrium, we expect that $\Omega_E(E_R)$ is maximised, and the same is true for the related quantities of S , so

$$p_{E_S} \propto \Omega_R(E_R) = \Omega_R(E - E_S).$$

Since $E_S \ll E$, Taylor expanding $\log \Omega_R$ gives

$$\begin{aligned}\log \Omega_R(E_R) &= \log \Omega_R(E) - \left. \frac{\partial \log \Omega_R}{\partial E_R} \right|_{E_R=E} E_S + \dots \\ &= \log \Omega_R(E) - \beta E_S + \dots,\end{aligned}$$

recalling that the entropy is $k_B \log \Omega$ and that $1/T = \partial S / \partial E = k_B \log \partial \Omega / \partial E$, as well as $\beta = \beta_R = \beta_S$ since they are thermally coupled and in equilibrium. Then taking an exponential of both sides and normalising results in

$$p_{E_S} = \frac{e^{-\beta E_S}}{\sum_S e^{-\beta E_S}}, \quad (2.14)$$

where we are summing over all accessible states in S . The factor $e^{-\beta E_S}$ is called the **Boltzmann factor**.

Taking the second approach, we view S as a member of \mathcal{E}_c . Assuming we have N identical systems labelled by i sharing energy E , the energy of a system r as E_r , and the number of states having this energy as n_r . Then

$$\sum_r n_r = N, \quad \sum_r E_r n_r = E.$$

For average energy U of each system, we have $E = NU$. We want to find the distribution of energy into the various systems $\{n_r\}$. The number of permutations of $\{n_r\}$ is given by

$$W(\{n_r\}) = \frac{N!}{\prod_r n_r!}.$$

All possible states of the ensemble, subject to the constraints, are all equally likely to occur, and so the frequency of occurrence of $\{n_r\}$ is proportional to $W(\{n_r\})$. The most probable distribution will be the one for which $W(\{n_r\})$ is maximised, and can be shown to be

$$n_r^* = C e^{-\beta E_r},$$

which is the same result above after normalising.

We see the average energy U can be expressed as

$$U = \langle E_r \rangle = p_r E_r = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = -\frac{\partial}{\partial \beta} \log \sum_r e^{-\beta E_r}.$$

Also recall that the Helmholtz free energy is $F(T, X_i) = U - TS$, and that $dF = -S dT - P dV + \mu dN$, so that $-S = \partial F / \partial T$. Then

$$U = F + TS = F - T \frac{\partial F}{\partial T} = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right) = \frac{\partial(F/T)}{\partial(1/T)} = \frac{\partial(\beta F)}{\partial \beta}.$$

Comparing the terms within the derivative, we have

$$\log \sum_r e^{-\beta E_r} = -\beta F = -\frac{F}{k_B T}, \quad (2.15)$$

which gives a basic relation between the macroscopic thermodynamics and microscopic statistical mechanics through F .

We define the **partition function** Z by

$$Z(T, V, N) = \sum_r e^{-\beta E_r}, \quad (2.16)$$

so that

$$F(T, V, N) = -k_B T \log Z. \quad (2.17)$$

The partition function sums over the states of the appropriate energy levels, and depends on V and N . The knowledge of Z completely specifies the thermodynamic properties of the system (since we then have F and thus all the other thermodynamic quantities).

Example For the entropy S , note that

$$\begin{aligned} \langle \log p_r \rangle &= \left\langle \log \left(\frac{e^{-\beta E_r}}{Z} \right) \right\rangle = \langle -\log Z - \beta E_r \rangle \\ &= -\log Z - \beta \langle E_r \rangle = \beta F - \beta U \\ &= -\frac{S}{k_B}, \end{aligned}$$

thus $S = -k_B \langle \log p_r \rangle = -k_B \sum_r p_r \log p_r$, as Z and β are fixed over the ensemble

Note that similarities with the **Shannon information entropy**
 $H = -\sum_r p_r \log p_r$.

The above demonstration implies that the entropy is completely specified by the probability distribution (given by the Boltzmann weights $e^{-\beta E_r}$). If the ground state of the system is unique then $S = 0$, as prescribed by the third law of thermodynamics. Physically this relates the entropy to the degree of uncertainty of the system, hence entropy is sometimes viewed as a measure of disorder. Note that for the case where only one E_r is available (i.e. fixed energy, so like in the micro-canonical ensemble) and $n_r = \Omega$,

$$S = -k_B \sum_r p_r \log p_r = -k_B \sum_r \Omega^{-1} \log \Omega^{-1} = -k_B \log \Omega^{-1} = k_B \log \Omega.$$

Consider a physical system that has some degeneracy where $g - i$ states have energy E_i . Then $Z = \sum_i g_i e^{-\beta E_i}$, and the probability of finding a state with energy E_i is (no sum)

$$p_i = \frac{1}{Z} g_i e^{-\beta E_i}.$$

If we can consider the system where the energy spacings are sufficiently fine, then we can talk about the probability of finding a state

with energy in $(E, E + \delta E)$ using the **density of states** $D(E)$, where $D(E) \, dE$ is the number of states in $(E, E + \delta E)$. With that,

$$p(E) \, dE = \frac{e^{-\beta E} D(E) \, dE}{\int_0^\infty e^{-\beta E} D(E) \, dE} = \frac{e^{-\beta E} D(E) \, dE}{Z(T)}$$

where $p(E)$ is the probability of finding the states with energy in the appropriate energy band. We note that the partition function $Z(T)$ as an integral is the Laplace transform of $D(E)$ with respect to β . This can be formally inverted as

$$D(E) = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} Z(\beta) e^{\beta E} \, d\beta, \quad (2.18)$$

where $\beta' > 0$, and the integral is taken in the usual sense for Laplace transform inversions. This is sometimes called the **Bromwich integral**.

2.2.1 Ensemble averages in \mathcal{E}_c

