

THERMODYNAMIC LIMIT AND EQUIVALENCE OF ENSEMBLES

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1 The thermodynamic limit

We recall from the previous lectures that the description of a large system is obtained in the **thermodynamic limit (TL)**, which is the limit for a large number N of particles where the volume of the vessel Λ which contains them is taken to grow in proportion with the number of particles. More precisely, the thermodynamic limit is defined as the limit of a system with a large volume V , with the particle density n and energy per particle e that are held fixed:

$$E, N, V, \Lambda \rightarrow \infty \quad \text{such that} \quad \frac{E}{N} \rightarrow e, \quad \frac{N}{V} \rightarrow n \quad \text{with } e, n \text{ finite.}$$

The prototypical **TL** is

$$\frac{1}{N} \log |\Gamma_{E, \delta E}| \rightarrow s(e, n) \quad \left(\text{equivalent notation: } |\Gamma_{E, \delta E}| \asymp e^{Ns(e, \varepsilon)} \right). \quad (1)$$

where $\Gamma_{E, \delta E}$ is the energy shell $E \leq H(x) \leq E + \delta E$. Once it is established that the limit $s(e, n)$ exists (and is finite!), one may use it for an asymptotic estimate of the microcanonical measure

$$\rho_E(x) d\Gamma = \begin{cases} \frac{1}{|\Gamma_{E, \delta E}|} d\Gamma & \text{if } E \leq H(x) \leq E + \delta E \\ 0 & \text{otherwise} \end{cases} \quad (2)$$

(where

$$d\Gamma = \frac{d^3 \mathbf{q}_1 \dots d^3 \mathbf{q}_N d^3 \mathbf{p}_1 \dots d^3 \mathbf{p}_N}{N! h^{3N}}.$$

In fact, the existence of the limit guarantees the goodness of the approximation

$$|\Gamma_{E, \delta E}| \approx e^{Ns(e, \varepsilon)} \quad (3)$$

The thermodynamic limit is essentially a consequence of the **law of large numbers**. The energy of a gas of N particles is the sum of order N contributions, each of which is approximately independent, and so the ratio of the size of the fluctuations to the mean is of order $1/\sqrt{N}$. Thus for a macroscopic volume with perhaps Avogadro's number

of particles, fluctuations are negligible, and so thermodynamics works. In general, almost all macroscopic volumes of gases, liquids and solids can be treated as being in the **TL**.

The existence of (1) is easily proved for the ideal gas; we have shown that

$$s(v, e) = N \left(\log v + \frac{3}{2} \log e + \frac{3}{2} \log \frac{4\pi m}{3h^2} + \frac{5}{2} \right) \quad (4)$$

which is indeed (a part from constants) the formula for the thermodynamic equilibrium entropy of an ideal mono-atomic gas. In a following lecture we shall argue why the identification between the logarithm of the volume of the energy shell and the equilibrium entropy is justified.

The natural question that arises is, Under what circumstances can we expect that the **TL** exists for a system of interacting particles?

In the calculation of $|\Gamma_{E, \delta E}|$ we need to specify, in principle, not only the value of the volume of our system, but also its precise form (for example a cylinder, a cube, a sphere), and in as this may influence the outcome. On the other hand, thermodynamics usually does not worry too much about these forms. For this to make sense, the **TL** should not be terribly dependent on the shape of the volumes of the systems along which the limit is taken. In fact, for systems with short range interactions, it can be shown that this is true provided that the volumes are reasonable, in the sense that the relationship between surface area and volume goes to zero.

For short-range interaction, we mean that the microscopic potential $\phi(r)$ of interaction between two particles at a distance r is of the form

$$\phi(r) = \phi_{hc}(r) + \phi_0(r) \quad (5)$$

where $\phi_{hc}(r)$ is the “hard core” potential

$$\phi_{hc}(r) = \begin{cases} 0 & \text{for } r > r_0 \\ \infty & \text{per } r \leq r_0, \end{cases} \quad (6)$$

The “ ∞ ” in above equation means that the particles can not approach among themselves at a distance less than r_0 , so that the particles can be regarded as rigid spheres in diameter $\sim r_0$. The potential ϕ_0 is a function which is smooth and short-range (for example, zero to a value of r large but finite or possibly tending exponentially to 0 when $r \rightarrow \infty$). For interactions of this type and with a proper characterization of the limit of infinite volume, which dates back to Léon van Hove (1950), it is possible to show that the **TL** exists; the full demonstration was given by David Ruelle (1963) and Michael Fisher (1964).¹

To demonstrate that the **TL** exists is not enough to ensure that the thermodynamic equilibrium of the system exists. It must also show that thermodynamics which is obtained in the limit is stable, that is to say, for example, that the compressibility and the thermal capacity are non-negative, and more generally that the entropy is concave. It turns out that for a interaction potential of the type (5) this is guaranteed and is, in effect, a by-product of the existence of the **TL**.

¹The existence of the **TL** for Coulomb interaction forces has been fixed in quite recent times by Dyson, Lenard, Lebowitz and Lieb.

When there is no thermodynamic limit

A thermodynamic limit does not exist in all cases. A noteworthy example is that of particles with an attractive potential which doesn't become repulsive even at very short distances: In such a case, matter tends to clump together instead of spreading out evenly over all the available space. This is the case for gravitational systems, where matter tends to clump into filaments, galactic superclusters, galaxies, stellar clusters and stars. Another possibility, studied in more recent years, is the case in which the limit exists, but the function $s(e, n)$ is non concave; this lack of concavity leads to global or local instabilities and an anomalous thermodynamic behavior. Unless otherwise stated, in the following we shall assume that the interaction potentials are such that the **TL** exists and the **function $s(e, n)$ is concave**.

2 The canonical distribution

In the previous lecture we have shown that the canonical distribution emerges when we study the properties of a subsystem of a large system and we take the **TL** limit. Now we want to reconsider the canonical distribution from a different point of view: as a convenient tool to approximate the microcanonical distribution of a large system.

Consider the the microcanonical distribution (2) and assume that the Laplace transform of $\Omega(E)$

$$Z(\lambda) = \int_0^{\infty} e^{-\lambda E} \Omega(E) dE = \int_{\Gamma} e^{-\lambda H(x)} d\Gamma \quad (7)$$

converges for any $\lambda > 0$ and define for any $\lambda > 0$ the canonical distribution

$$\rho_{\lambda}(E) = \frac{1}{Z(\lambda)} e^{-\lambda E} \Omega(E) \quad (8)$$

$$\rho_{\lambda}(E) \geq 0, \quad \int \rho_{\lambda}(E) dE = 1$$

Thus, $\rho_{\lambda}(E)$ is a probability density for any $\lambda > 0$.

Our goal is to show that there exist a suitable λ for which the canonical distribution approximates to any desired accuracy the microcanonical distribution. But before doing that we review some properties of the canonical distribution.

3 The partition function

The function $Z(\lambda)$ is called the partition function. If we assume that $\Omega(E)$ is **positive and monotonically increasing for $E > 0$** , it is quite easy to see that

- (a) $Z(\lambda)$ is a positive and monotonically decreasing function of λ .
- (b) $Z(\lambda) \rightarrow \infty$ for $\lambda \rightarrow 0$.
- (c) For any $\lambda > 0$, $Z(\lambda)$ has derivatives of all orders. For $n = 1, 2, \dots$

$$Z^{(n)}(\lambda) = (-1)^n \int E^n e^{-\lambda E} \Omega(E) dE \quad (9)$$

Given the partition function, the moments of the energy H are immediately obtained by means of (9):

$$\mathbb{E}_{\lambda}\{H^n\} = (-1)^n \frac{Z^{(n)}(\lambda)}{Z(\lambda)}.$$

In particular, mean value and variance are:

$$\mathbb{E}_\lambda\{H\} = \frac{1}{Z(\lambda)} \int E e^{-\lambda E} \Omega(E) dE = -\frac{Z'(\lambda)}{Z(\lambda)} = -\frac{d \log Z(\lambda)}{d\lambda} \quad (10)$$

$$\text{Var}_\lambda(H) = \langle H^2 \rangle - \langle H \rangle^2 = \frac{Z''(\lambda)}{Z(\lambda)} - \left(\frac{Z'(\lambda)}{Z(\lambda)} \right)^2 = \frac{d^2 \log Z(\lambda)}{d\lambda^2} = -\frac{d \langle H \rangle}{d\lambda} \quad (11)$$

4 Composition law for weakly interacting systems

The most important property of partitions functions is their law of composition, i.e. the law by which the partition function is constructed from the partition functions of its components.

Let the system consist of two weakly interacting components a and b with densities of states $\Omega_a(E)$ and $\Omega_b(E)$, and partition functions $Z_a(\lambda)$ and $Z_b(\lambda)$. Since,

$$\Omega(E) = \int \Omega_a(E_a) \Omega_b(E - E_a) dE_a$$

(we have omitted the dependence on the the number of components which are assumed to be fixed), from the known properties of the Laplace transform, we have

$$Z(\lambda) = Z_a(\lambda) Z_b(\lambda) \quad (12)$$

Thus if we consider a gas of N particles with negligible interaction among them, and $z(\lambda)$ is the partition function of a single particle, then the partition function of the gas is

$$Z(\lambda) = \frac{1}{N!} z(\lambda)^N$$

(the factor in front because the particle are identical).

The law of composition of the density of states together with the definition of the canonical distribution, gives us

$$\rho_\lambda(E) = \int \rho_a(E_a) \rho_b(E - E_a) dE_a \quad (13)$$

This means that H_a and H_b whose sum is the total energy $H = H_a + H_b$ are **independent random variables**, that is, that the joint probability distribution $\rho_\lambda(E_a, E_b)$ factorizes:

$$\rho_\lambda(E_a, E_b) = \rho_a^{(\lambda)}(E_a) \rho_b^{(\lambda)}(E_b) \quad (14)$$

Systems consisting of a large number of components Formula (14) can be generalized to the important case where the system consists of any number n of weakly interacting components with energy function

$$H = h_1 + \dots + h_n.$$

We are thus led to the following rule concerning the composition of the canonical distributions: **The canonical distribution law of a given system consisting of n weakly inreacting components can be derived from the corresponding distributions of its n components in the same way as the distribution of a sum of n mutually independent random quantities is found from the distributions of individual terms.** It is clear that the value of the parameter λ is quite arbitrary, but must be the same for all systems in question.

5 Canonical distribution of the ideal gas

For an ideal gas of N identical particles the energies h_k are independent r.v. which are identically distributed as the single particle Hamiltonian

$$h = \frac{|\mathbf{p}|^2}{2m}$$

The single particle partition function is

$$z(\lambda) = \frac{V}{h^3} \int dp_x dp_y dp_z e^{-\lambda (p_x^2 + p_y^2 + p_z^2)/(2m)} = V \left(\frac{2\pi m}{h^2 \lambda} \right)^{3/2}$$

whence the partition function of the gas:

$$Z(\lambda) = \frac{1}{N!} z(\lambda)^N = \frac{1}{N!} V^N \left(\frac{2\pi m}{h^2 \lambda} \right)^{3N/2}$$

For N large, using Stirling as usual, we obtain

$$\log Z(\lambda) = N \log \left[\frac{V}{N} \left(\frac{2\pi m}{h^2 \lambda} \right)^{3/2} \right] + N$$

Thus

$$\lim_{N \rightarrow \infty} \frac{1}{N} \log Z(\lambda) = \psi(n, \lambda) \quad (15)$$

with

$$\psi(n, \lambda) = \log v + \frac{3}{2} \log \frac{1}{\lambda} + \frac{3}{2} \log \frac{2\pi m}{h^2} + 1, \quad (16)$$

i.e.,

$$Z(\lambda) \asymp e^{N\psi(n, \lambda)} \quad (17)$$

It is instructive to compute the asymptotic mean and variance of the energy. From (10) we obtain

$$\begin{aligned} \mathbb{E}_\lambda\{H\} &= -\frac{d \log Z(\lambda)}{d\lambda} = \frac{dN\phi}{d\lambda} = \frac{d}{d\lambda} \left(\frac{3N}{2} \log \lambda \right) = \frac{3N}{2\lambda} \\ \text{Var}_\lambda(H) &= -\frac{d\mathbb{E}_\lambda\{H\}}{d\lambda} = \frac{3N}{\lambda^2} \end{aligned}$$

whence

$$\mathbb{E}_\lambda \left\{ \frac{H}{N} \right\} = \frac{3}{2\lambda} \equiv e \quad (18)$$

$$\text{Var}_\lambda \left(\frac{H}{N} \right) = \frac{3}{\lambda^2 N} \quad (19)$$

Thus, asymptotically, the empirical mean $h = H/N$ concentrates on the theoretical mean e (Law of the Large Numbers), with normal fluctuations around it (Central Limit Theorem).

Finally, observe that when we use (18) to express λ in terms of e , i.e., we write $\lambda = 3/(2e)$, and insert it in (16), we obtain

$$\begin{aligned} \psi(n, e) &= \log v + \frac{3}{2} \log \frac{2e}{3} + \frac{3}{2} \log \frac{2\pi m}{h^2} + 1 \\ &= \log v + \frac{3}{2} \log e + \frac{3}{2} \log \frac{4\pi m}{3h^2} + 1 \end{aligned}$$

Comparing this formula with the formula (4) for the entropy, we see that s and ϕ differ just for factor $3/2$, that is $\phi = 3/2 - s$. But $3/2$ is nothing but λe , so that we have

$$\phi = s - \lambda e \quad (20)$$

This formula is far from accidental and it turns out to be true for more general systems, provided the **TL** is finite and s is concave.

6 Thermodynamic limit

Suppose now that Z/N has a finite **TL**, i.e., for $N/V \rightarrow n$ and fixed λ

$$\lim_{N \rightarrow \infty} \frac{1}{N} \log Z(\lambda) = \psi(\lambda, n) \quad (21)$$

where ψ is a “nice” function. Then for the mean $h = H/N$ we obtain

$$\mathbb{E}_\lambda \{h\} \rightarrow -\frac{d}{d\lambda} \lim_{N \rightarrow \infty} \frac{1}{N} \log Z(\lambda) = -\frac{\partial \psi(\lambda, n)}{\partial \lambda} \equiv e \quad (22)$$

(assuming uniformity of the limit). Since

$$\text{Var}_\lambda (H) = -\frac{d \langle H \rangle}{d\lambda} \rightarrow -N \frac{de}{d\lambda}$$

$$\text{Var}_\lambda (h) = \frac{\text{Var}_\lambda (H)}{N^2} \rightarrow -\frac{1}{N} \frac{de}{d\lambda} = \frac{1}{N} \frac{\partial^2 \psi(\lambda, n)}{\partial \lambda^2} \rightarrow 0$$

Thus we see that for the empirical mean of energy $h = H/N$ the **LLN** and the **CLT** hold true: the distribution of h gets concentrated around the asymptotic theoretical mean e with normal fluctuations around the mean (indeed we did not prove the CLT, but only controlled the normal behavior of the the variance).

7 Equivalence of microcanonical and canonical distributions

Euristics Consider the partition function for finite N

$$Z_N(\lambda) = \int_0^\infty e^{-\lambda E} \Omega_N(E) dE$$

(for simplicity forget the dependence on V).

Assume that

(a) the **TL** of $\Omega_N(E)$ is finite, i.e.

$$\Omega_N(E) \asymp e^{Ns(\frac{E}{N})}$$

(b) $s(\varepsilon)$ is a smooth concave function.

Then

$$Z_N(\lambda) \sim \int_0^\infty e^{-\lambda E} e^{Ns(\frac{E}{N})} dE = \int_0^\infty e^{-\lambda N\varepsilon} e^{Ns(\varepsilon)} d\varepsilon = \int_0^\infty e^{N[-\lambda\varepsilon + s(\varepsilon)]} d\varepsilon$$

By Laplace’s method of asymptotic evaluations of integrals we obtain

$$Z(\lambda) \asymp e^{N \sup_\varepsilon \{s(\varepsilon) - \lambda\varepsilon\}}$$

Assumption (b) guarantees that there is only one value of ε maximizing $F(\lambda, \varepsilon) = s(\varepsilon) - \lambda\varepsilon$. Let e be such a value. Then $e = e(\lambda)$ is the solution of the equation

$$\lambda = \frac{\partial s(e)}{\partial e} \quad (23)$$

and thus

$$\psi(\lambda) = s(e(\lambda)) - \lambda e(\lambda) \quad (24)$$

But under the assumption of concavity of s , equation (23) can be solved with respect to $\lambda(e)$. In this way we obtain

$$s(e) = \lambda(e)e + \psi(\lambda(e)) \quad (25)$$

In other words, $s(e)$ and $\psi(\lambda)$ are one-to-one related by a Legendre transformation:

$$\psi(\lambda) = \sup_e [s(e) - \lambda e] \quad (26)$$

$$s(e) = \inf_\lambda [\lambda e + \psi(\lambda)] \quad (27)$$

Note that the value of $\lambda = \lambda(e)$ that minimize $\lambda e - \psi(\lambda)$ can also be expressed as the solution of the equation

$$e = \frac{d\psi}{d\lambda} \quad (28)$$

(Legendre duality) and thus, recalling (22), as the solution of the equation

$$e = \mathbb{E}_\lambda\{h\}. \quad (29)$$

The asymptotic equivalence of the microcanonical and canonical ensembles is thus established: given a microcanonical distribution of energy E (with some tolerance δE), the canonical distribution with value of the parameter λ which solves equation (29), provides, in the **TL** the same statistics of the microcanonical one.

The equivalence breaks down when s is not concave (see the beginning of the lecture).