

EQUILIBRIUM STATISTICAL MECHANICS

Contents

1 The fundamental equation of equilibrium statistical mechanics	1
2 Conjugate representations	2
3 General overview on the method of ensembles	4
4 The relation micro-macro	4
5 Einstein's Statistical Thermodynamics	5
6 Einstein's discovery of the photon	5

1 The fundamental equation of equilibrium statistical mechanics

Let us summarize where we stand. On one hand, we have the microscopic description of a system given by its microstate, on the other hand its macroscopic description given by the macroscopic variables. Let us focus on a simple fluid of N particles confined in a container Λ of volume V . The microstate is described by a point in phase Γ and its time evolution governed by its Hamiltonian

$$H(x) = \sum_{i:q_i \in \Lambda} \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{i,j:q_i, q_j \in \Lambda} \phi(|q_i - q_j|) = E \quad (+ \text{ boundary conditions}) \quad (1)$$

takes place on the shell of constant energy Γ_E (with some tolerance δE). The boundary conditions ensure that the number of particles $N(x)$ stays constant:

$$N(x) = \sum_{i:q_i \in \Lambda} 1 = N. \quad (2)$$

The macroscopic description of the system is in terms of the macroscopic variables, describing, say, the energy and the number of particles of subsystems (as we have seen in previous lectures). The macroscopic variables induces a partition of phase space and the equilibrium macrostate corresponds to the values of the macroscopic variables whose associated region in phase space, Γ_{eq} , is the the largest one, indeed, Γ_{eq} is exponentially larger in the number of particles with respect to any another region in the energy shell Γ_E . Thus, for the Boltzmann's entropy of the equilibrium macrostate we have

$$S_B = \log |\Gamma_{eq}| \approx \log |\Gamma_E|. \quad (3)$$

This introduces an enormous simplification in studying the equilibrium properties of a system!

Let us make explicit the dependence of $|\Gamma_{eq}|$ on the **microcanonical constraint** (1) and (2):

$$|\Gamma_{eq}| = \Omega_\Lambda(E, N) \quad (4)$$

The thermodynamic limit is a limit in which the region $\Lambda \rightarrow \infty$, in the sense that it expands to all physical space, this means, in particular that $V = |\Lambda| \rightarrow \infty$. Moreover

$N \rightarrow \infty$, while keeping constant $E/N = e$ and $N/v = n$. For the physical pair potential of a fluid (short range) it has been shown that the limit

$$\lim_{\substack{N \rightarrow \infty, V \rightarrow \infty \\ E/N=e, N/V=n}} \log \Omega_{\Lambda}(E, N) = s(e, n) \quad (5)$$

exists and $s(e, n)$ is a concave function of its arguments. This function is used as an excellent approximation of the entropy of a finite system:

$$S_{\text{eq. micro}}(E, V, N) = Ns\left(\frac{E}{N}, \frac{N}{V}\right) \quad (6)$$

we have written S_{micro} to emphasize that it is determined by the microscopic structure of the system. It has (under the stated assumptions) all the properties of the thermodynamic equilibrium entropy $S_{\text{eq. macro}}(E, V, N)$. Thus, we have the identification

$$S_{\text{eq. macro}} = S_{\text{eq. micro}} \quad (7)$$

This is the ***fundamental equation of equilibrium statistical mechanics***. Then the basic postulate of equilibrium thermodynamics is so established:

Proposition 1

There is a function, called entropy, of the extensive variables of any composite system, which is defined for all equilibrium macrostates and has the following properties: 1) the values of the variables in the absence of extensive internal constraints are those that maximize the entropy on the set of the constrained equilibrium macrostates; 2) the entropy of a composite system is the sum of the entropies of its subsystems. Entropy is a monotonically increasing function of energy.

From now on we shall drop the indices and write simply $S = (E, V, N)$. This function is in principle computable from the microscopic description of a system. And once this function is known, we have complete thermodynamic information about the system. It is usually called the fundamental equation of a system. Its differential form

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN, \quad (8)$$

is the so-called Gibbs equation in the entropy representation.

2 Conjugate representations

The conjugate representations or are obtained by relaxing the microcanonical constraints and use canonical distributions of H and N whose means are equal to the microcanonical constraints. Then, in the thermodynamics limit, one obtains an equivalent thermodynamic representation of the properties of a system.

If both constrains are relaxed, neither energy nor the particles numbers are fixed. So one represents the system in the phase space with a variable numbers of particle

$$\Gamma_{\Lambda} = \bigcup_{K=0}^{\infty} \Gamma_{\Lambda, K}$$

where $\Gamma_{\Lambda,K}$ is the phase space K particles in Λ . The corresponding canonical distribution is characterized by its partition function

$$Z_V(\lambda_0, \lambda_1) = \sum_{K=0}^{\infty} \int e^{-\lambda_0 H_K(x) - \lambda_1 K} \frac{d^{3K}x}{h^{3K} N!}. \quad (9)$$

the so called **grand canonical partition function**. The parameters λ_0, λ_1 are determined by the condition that in the thermodynamic limit the microcanonical constraints are restored.

The thermodynamic limit now assumes the form

$$\lim_{\substack{V \rightarrow \infty \\ \lambda_0, \lambda_1 \text{ fixed}}} \frac{\log Z_V(\lambda_0, \lambda_1)}{V} = \psi(\lambda_0, \lambda_1) \quad (10)$$

In previous lectures we have shown that the Massieu function $\Psi(V, \lambda_0, \lambda_1) = N\psi(\lambda_0, \lambda_1)$ is in one-to-one correspondence with the entropy $S(E, N, V)$ via a Legendre transformations:

$$\Psi(\lambda_0, \lambda_1) = \sup_{E, N} [S(E, N, V) - \lambda_0 E - \lambda_1 N] \quad (11)$$

$$S(E, N, V) = \inf_{\lambda_0, \lambda_1} [\lambda_0 E + \lambda_1 N + \Psi(\lambda_0, \lambda_1)] \quad (12)$$

But the thermodynamic Massieu function is

$$\Psi(V, \beta, \mu) = \sup_{E, N} [S(E, N, V) - \beta E - \beta \mu N] \quad (13)$$

and so we have the identifications

$$\lambda_0 = \beta = \frac{1}{T} \quad (14)$$

$$\lambda_1 = -\beta \mu = -\frac{\mu}{T} \quad (15)$$

For these values of the parameters λ_0, λ_1 , there is complete equivalence of the grand canonical ensemble, defined by the partition function,

$$Z_{\Lambda}(\beta, \mu) = \sum_{K=0}^{\infty} \int e^{-\beta H_K(x) + \mu K} \frac{d^{3K}x}{h^{3K} K!}, \quad (16)$$

with the microcanonical one defined by E and N given by

$$E = -\frac{\partial \log Z_{\Lambda}(\beta, \mu)}{\partial \beta} \quad (17)$$

$$N = -\frac{\partial \log Z_{\Lambda}(\beta, \mu)}{\partial(-\beta \mu)} = \frac{1}{\beta} \frac{\partial \log Z_{\Lambda}(\beta, \mu)}{\partial \mu} \quad (18)$$

$$(19)$$

Traditionally, people prefer to work with potentials Φ instead of Massieu functions Ψ , the relation between the two being

$$\Phi = -\frac{1}{\beta} \Psi. \quad (20)$$

The potential related to (13) is the so-called Landau potential.

Sometimes one writes

$$Z_V(\beta, \mu) = \sum_{K=0}^{\infty} \varkappa^K Z_V(\beta|K)$$

where

$$\varkappa = e^{\beta\mu} \tag{21}$$

is the so-called **fugacity** and

$$Z_V(\beta|K) = \int e^{-\beta H_K(x)} \frac{d^{3K}x}{h^{3K} K!} \tag{22}$$

is the so-called the **canonical** partition function.

3 General overview on the method of ensembles

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4 The relation micro-macro

Let us go back to what we have called the the **fundamental equation of equilibrium statistical mechanics**, namely

$$S_{\text{macro}} = S_{\text{micro}}$$

(we have dropped the qualificatio “eq.”, because this relation holds more generally, al so for non equilibrium). One may wonder on the status of this relationship.

In some cases, we are able compute S_{micro} and thus to derive the macroscopic behavior of a system from its microscopic description and thus “proving”

$$\text{micro} \rightarrow \text{macro} . \tag{23}$$

However, we are able to (partly) achieve this only under some (not always understood) approximation (e.g., dilute gas, Boltzmann) or for very idealized models (e.g., Ising models and lattice gases). But also when we do this, we some key steps in the arrow above are still out of reach (phase transitions). Another way to go from the micro to the macro is to assume that the microscopic Hamiltonians is generic (or typical) in some class (this method was put forward by Wigner).

Be that as it may, for **realistic systems, that is systems governed by realistic Hamiltonians**, the arrow $\text{micro} \rightarrow \text{macro}$ is out of reach.

There is the other arrow, put forward and used at large by Einstein:

$$\text{micro} \leftarrow \text{macro} . \tag{24}$$

This means to use the macroscopic information available from experimental research in oder to draw conclusion on the microscopic behavior.

All the effective practice of statistical mechanics is a combination of the two arrows,

$$\text{micro} \rightleftharpoons \text{macro} ,$$

done, as Nero Wolfe would say, with our “intelligence guided by experience.”

5 Einstein's Statistical Thermodynamics

Einstein inverted the Boltzmann relationship between entropy and probability and considered this relationship as a phenomenological definition of the probability of a deviation from equilibrium. We call this *Einstein postulate*. The theory that arises from this postulate—statistical thermodynamics—can be considered as a theory on its own. The whole theory is based on the following postulate.

Proposition 2 (Einstein's postulate)

Let Y be a parameter (or several such parameters) that describes an isolated system, so that its total energy is constant and its entropy function is $S_{\text{tot}}(Y)$. If the parameter Y is free to vary, then the fundamental statistical postulate asserts that in an equilibrium situation the probability \mathbb{P} of finding the system with the parameter between Y and $Y + dY$ is given by

$$\mathbb{P}(Y \leq Y \leq Y + dY) = C e^{S_{\text{tot}}(Y)} dY \quad (25)$$

where C is a normalization constant.

General comments on Einstein's postulate

- Physical quantities which describe a macroscopic body in equilibrium are, almost always, constant and governed by thermodynamics. However, in the course of time, deviations from these values, though small, do occur and the quantities are said to *fluctuate*. Eq. (25) gives the probability of these deviations. $Y = Y(x)$ is a function of the micro-state that provide the complete microscopic description of the system.
- From a mathematical point of view, this means that a thermodynamic variable Y is now regarded as a random variable Y (or several such variables), whose values Y are distributed according the probability law (25).
- The physically relevant application of Einstein's postulate is to the variables that describe the fundamental thermodynamic quantities of any small part of a large system. This small part should still contain, however, a sufficiently large number of particles. For quantities such as energy and volume, which have a pure mechanical meaning, as well as a thermodynamic one, the concept of fluctuation is clear, but it needs more precise qualification for quantities such as entropy and temperature. For example, let $S(E, V)$ be the equilibrium quantity of a body as function of its thermodynamic energy and volume. By fluctuation of the entropy, we shall mean the change in the function $S(H, V)$, regarded as a function of the microscopic values of energy H and volume V .

6 Einstein's discovery of the photon

We follow Dennis Sciama¹

¹*Black holes and fluctuations of quantum particles: an Einstein synthesis* (1979). In *Relativity, quanta and cosmology*, ed. M. Pantaleo & F. de Finis (Johnson Reprint Corporation), p. 681.

It was characteristic of Einstein's approach to statistical mechanics that he took for granted the equality of time averages and phase averages. Now, according to the Boltzmann distribution, when a large number of systems are in thermal equilibrium at temperature T , the number of systems with energy E is proportional to $e^{-E/kT}$. Einstein therefore assumed that a single system would have an energy E for a fraction $e^{-E/kT}$ of the time. He applied this assumption to the black-body energy in a fixed unit volume, and immediately obtained the result

$$\overline{\Delta\epsilon_\nu^2} = -k \left(\frac{\partial \bar{\epsilon}_\nu}{\partial(1/T)} \right)_\nu$$

Now, according to the Planck law,

$$\bar{\epsilon}_\nu = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1}$$

Hence Einstein obtained the basic result

$$\overline{\Delta\epsilon_\nu^2} = h\nu \bar{\epsilon}_\nu + \frac{c^3 \bar{\epsilon}_\nu^2}{8\pi\nu^2 d\nu} \quad (1)$$

...

What impressed Einstein most about his fluctuation formula (1) is that it consisted of two terms, one linear in the energy density and one quadratic. He saw that the quadratic term had an immediate interpretation in terms of a classical wave model for the electromagnetic radiation field. Regarding thermal radiation as a statistical mixture of harmonic waves with a random distribution of phases, one would expect interference effects to give rise to localized fluctuations of energy. At each frequency these fluctuations would be proportional to the square of the radiation intensity at that frequency. In fact one can calculate these fluctuations directly, without using thermal concepts, by averaging interference expressions over time and an assumed random distribution of phases. A detailed calculation of this type was carried out by Lorentz (1911, 1916), who obtained the result

$$\overline{\Delta\epsilon_\nu^2} = \bar{\epsilon}_\nu^2$$

for one mode of any state with random phases, whether thermal or not. [For a more accessible calculation in one spatial dimension, see Tomonaga (1962).]

To explain the linear term Einstein introduced the hypothesis that each mode of frequency ν of the radiation field could also be regarded as made up of localized particles, or photons, of energy $E = h\nu$. If these particles move independently one would expect the probable number in a fixed volume to have a Poisson distribution, so that

$$\overline{\Delta n_\nu^2} = \bar{n}_\nu$$

or

$$\overline{\Delta \epsilon_\nu^2} = h\nu \bar{\epsilon}_\nu$$

Notice in particular that the wave and particle models must both be used at the same time (rather than as alternatives) and that they must be independent (since the mean square fluctuations associated with each model combine linearly). This puzzling aspect of the wave-particle model was clarified many years later when a more thoroughgoing quantum treatment of waves and particles was given.

5. The Quantum Particle Model

The Poisson distribution that Einstein used in 1905 assumes that the particles are distinguishable from one another. This would be reasonable in a classical model, but in 1924 Bose pointed out that this distinguishability might not hold quantum mechanically. Accordingly, Einstein recalculated the particle fluctua-

tions, assuming that the particles were indistinguishable but otherwise independent. He then obtained

$$\overline{\Delta n_\nu^2} = \bar{n}_\nu(1 + \bar{n}_\nu)$$

so that

$$\overline{\Delta \epsilon_\nu^2} = h\nu \bar{\epsilon}_\nu + \bar{\epsilon}_\nu^2$$

for one mode. We thus retrieve the quadratic term in a purely particle model. Here it owes its origin to an effective attraction in frequency space, which results from the statistics of indistinguishability.

2. The Planck Spectrum as an Interpolation Formula

At the time when Planck was seeking a precise expression for the black-body spectrum empirical approximations were known at low and high frequencies, namely, the Rayleigh–Jeans spectrum at low frequencies

$$\bar{\epsilon}_\nu = \frac{8\pi\nu^2}{c^3} kT$$

and the Wien spectrum at high frequencies

$$\bar{\epsilon}_\nu = \frac{8\pi h}{c^3} \nu^3 e^{-h\nu/kT}$$

where h was a purely empirical constant. Planck set about to discover a suitable interpolation formula that would hold for all values of the frequency.

Planck's solution was published in 1900. Five years later Einstein modified Planck's method (which used the entropy as an interpolating variable) by using his formula for the fluctuations. In the Rayleigh–Jeans part of the spectrum we have for one mode of mean energy $\bar{\epsilon} = kT$,

$$\overline{\Delta\epsilon^2} = kt^2 \frac{\partial \bar{\epsilon}}{\partial T} = \bar{\epsilon}^2$$

On the other hand, in the Wien part of the spectrum where one mode has mean energy $\bar{\epsilon} = h\nu e^{-h\nu/kT}$ we have

$$\overline{\Delta\epsilon^2} = h\nu\bar{\epsilon}$$

These two different expressions for the fluctuations suggest that two different causes are at work that predominate at low and high frequencies, respectively.

Einstein made the provisional assumption that these two causes acted independently, and so he simply added together their mean square fluctuations for a general frequency when both causes operated simultaneously. This would give

$$\overline{\Delta\epsilon^2} = kT^2 \frac{d\bar{\epsilon}}{dT} = \bar{\epsilon}^2 + h\nu\bar{\epsilon}$$

The general solution of this differential equation is

$$\bar{\epsilon} = \frac{h\nu}{e^{(h\nu - m_0)/kT} - 1} \quad (3)$$

from which the Planck spectrum for all modes follows:

$$\bar{\epsilon}_\nu = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1}$$

since the constant of integration m_0 must be set equal to zero to retrieve the Rayleigh–Jeans and Wien approximations.