Crash course on statistical physics

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Ludwig Boltzmann, who spent much of his life studying Statistical Mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study Statistical Mechanics.

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1 Thermodynamics in one phrase and goal of statistical physics

Thermodynamics. In the macroscopic world one knows that, for a system with fixed energy, volume, and number of bodies, E, V, N, respectively, there is a function (a *thermodynamic potential*), S(E, V, N), the entropy, whose derivatives provide the functions temperature, pressure and chemical potential: $dS = T dE + P dV + \mu dN$, all of them functions of (E, V, N). In different ensembles, when T, V, N or T, P, N or T, P, μ , or other combinations are fixed, the quantities that are not fixed are functions of those that are fixed (E(T, V, N) for example) and can be obtained as the derivatives of the corresponding thermodynamic potential, in its turn obtained from S by the corresponding Legendre¹ transformations:

$$E, V, N \qquad S \qquad T \, \mathrm{d}S = \mathrm{d}E + P \, \mathrm{d}V + \mu \, \mathrm{d}N \qquad (1.1)$$

-1T

$$T, V, N \qquad F = E - TS \qquad dF = -S dT - F dV + \mu dN \qquad (1.2)$$
$$T, P, N \qquad G = F + PV \qquad dG = -S dT + V dP + \mu dN \qquad (1.3)$$

 $C \downarrow T = D \downarrow U + \dots \downarrow N$

(1 0)

and so on.

TUN

The thermodynamic potentials cannot be any function. They are different for different physical systems, but for any system they are subject to some conditions reflecting the thermodynamic equilibrium of the system they represent: these conditions are extremmum conditions with respect to the introduction (or release) of constraints in the system. In the E, V, N (microcanonical) ensemble, if one divides the system into two subparts which can exchange volume $V = V_1 + V_2$ (by a free piston), modifying the position of the piston and changing the volume V_1 with respect to its most probable value (i.e., that with the piston let free) will *lower* the corresponding microcanonical entropy. *Mutatis mutandis* for E and N. In the microcanonical ensemble, hence, S is a maximum with respect to the removal of constraints. This translates (check it!) into the stability conditions in the microcanonical ensemble:

$$(\partial_E \beta)_V < 0 \qquad (\partial_V P)_E < 0 \tag{1.4}$$

Throught the Legendre transformations (1.3) one can deduce the stability conditions in different ensambles. The thermodynamic potential of each of them can be either a maximum of a minimum with respect to the removal of internal constraints.

¹Remember, f is the Legendre transformation of e if $f(t) = e(s^*(t)) - ts^*(t)$ where s^* is such that $e'(s^*(t)) = t$.

Aim of statistical mechanics. One would like to *calculate* the thermodynamic functions and potentials in different ensembles (which are functional relations between *macroscopic* quantities, as P(T, V, N)), provided the details of the interaction energy between the (many) *microscopic* bodies composing the system. The microscopic interaction is described by the pairwise interaction energy between two bodies, $\mathcal{H}_1[\sigma^{(1)}, \sigma^{(2)}]$, from which one constructs the Hamiltonian $\mathcal{H}[\boldsymbol{\sigma}] = \sum_{1 < i < j < N} \mathcal{H}_1[\sigma^{(i)}, \sigma^{(j)}]$, describing the total interaction energy of the configuration $\boldsymbol{\sigma} = \otimes_j \sigma^{(j)}$. In other words, the Hamiltonian is a functional over the *phase space* $\boldsymbol{\Sigma} = \{\boldsymbol{\sigma}\}$ (say, in a gas, the set of all positions and momenta of all the particles) of microscopic degrees of freedom composing the macroscopic system.

Along the way, statistical mechanic techniques may provide or estimate a probability measure, p_{EVN} (say), in the phase space, so that it may be possible to compute expectation values of different functionals (as correlators) $\mathcal{A} : \Sigma \to \mathbb{R}$, as $\langle \mathcal{A} \rangle_{EVN}$, where $\langle \cdot \rangle_{EVN}$ is performed according to p_{EVN} .

Generality. Pressure, volume and chemical potential are quantities relevant in the description of a fluid, but all this is general, valid for any kind of thermodynamic variable. For a magnetic system, all the reasonings above and below remain valid with the substitution:

$$m \leftrightarrow v \qquad h \leftrightarrow -P \tag{1.5}$$

where m is the magnetization and h is the magnetic field.

2 Statistical ensembles in a nutshell

Microcanonical ensemble. Consider a system with fixed energy, volume, and mass (numer of particles) given by E, V, N respectively (from now on we will suppose constant the number of particles N). The microcanonical ensemble is given by a probability measure on the microstates Σ , such that all states with a given energy are equiprobable:

$$p_{E,V,N}(\boldsymbol{\sigma}) = \frac{\delta(\mathcal{H}[\boldsymbol{\sigma}] - E)}{\Omega(E, V, N)}, \qquad \Omega(E, V, N) = \sum_{\boldsymbol{\sigma} \in \mathcal{V}_{V,N}} \delta(\mathcal{H}[\boldsymbol{\sigma}] - E)$$
(2.1)

where $\Omega(E, V, N)$ is the microcanonical partition function normalizing the probability density, or the number of microstates $\boldsymbol{\sigma}$ with N particles, enclosed in a volume V satisfying the constraint $\mathcal{H}[\boldsymbol{\sigma}] = E^2$. The microcanonical entropy and inverse temperature $\beta = 1/T$ are defined as:

$$S_{\rm m}(E,V,N) = \ln \Omega(E,V,N), \qquad \beta(E,V,N) = \partial_{E'} S_{\rm m}(E',V,N)|_E \tag{2.2}$$

Statistical physics identifies the (E, V, N)-ensemble thermodynamic potential S appearing in 1.3 with the function $S_{\rm m}$ defined in the precedent equation, linking in this way the microscopic to the macroscopic. Why so? Suppose that there is free piston letting the volume of a spatial partition, 1, of our system to be $V_1 \equiv N_1 v_1$ (the reasoning is identical for E, N). Ommitting the E, N dependence, it is: $\Omega = \int dv_1 \exp(N(s_1(v_1) + s_2(v - v_1))))$, where $N_1 s_1$ is the function S corresponding to subsystem 1 and so with 2. For large N, this function is very peaked on the maximum, let us call it v_1^* of the exponent, let us call it $s(v; v_1) = s_1(v_1) + s_2(v - v_1)$. $S_{\rm m}$ is, hence, an extensive function, maximum with respect to "internal constraints", and can be identified with the thermodynamic entropy defined in the last section (up to a (Boltzmann) constant). The maximum of the microcanonical entropy (2.2) signifies that the value of the internal constraints is the most probable one, i.e., is such that the number of microstates, $\exp[Ns(v; v_1^*)]$, compatible with the value v_1^* is maximum. The most probable value is exponentially much more probable than the rest, being N the coefficient in the exponential. ³

$$S(E, V, N) = N s(\epsilon, v) \qquad \epsilon = E/N \qquad v = V/N$$
(2.3)

and the same for the potentials F = fN and G = gN. In other ensembles, we do the same with the extensive functions (for example, $\epsilon(T, v) = E(T, V, N)/N$).

 $^{^{2}}$ The sum over microstates is symbolic, and it is to be regularized (quantum-mechanically) in the case of continuous degrees of freedom.

³ We have introduced the intensive entropy s = S/N. An implicit assumption is that, for sufficiently large N, the quantity S(E, V, N)/N do not depend on N, a fact which is guaranteed if the Hamiltonian meets some requirements. In this circumstance we define:

Canonical ensemble. Consider two systems 1 + 2 in the microcanonical ensemble at energy $E_{12} = E_1 + E_2$, E_1 being much lower than E_2 . Supposing also that they are short-range interacting so that their partition functions can be factorised, it is (we ommit the V, N dependence, indicating $\Omega(E_1, V_1, N_1)$ by $\Omega_1(E_1)$):

$$\Omega(E) = \int dE_1 \,\Omega_1(E_1)\Omega_2(E_2) = \tag{2.4}$$

$$\Omega_2(E) \int dE_1 \,\Omega_1(E_1) e^{-\beta E_1} = \Omega_2(E) \sum_{\boldsymbol{\sigma} \in \mathcal{V}_1} e^{-\beta \mathcal{H}[\boldsymbol{\sigma}]}$$
(2.5)

where we have Taylor expanded to first order in E_1 , where $\beta \equiv \partial_E S_m(E)|_{E_{12}}$ and where the sum is over the N_1 degrees of freedom belonging to the first partition $\mathcal{V}_1 \subset \Sigma$ (with volume V_1). The last factor of (2.5), depending only on subsystem 1, is the *canonical partition function* of 1, characterizing it (the whole dependence on the reservoire is in β , $\Omega(E) = \Omega_2(E)Z(\beta, V_1, N_1)$):

$$Z(\beta, V_1, N_1) = \int dE_1 \,\Omega_1(E_1, V_1, N_1) e^{-\beta E_1} = \sum_{\sigma \in \mathcal{V}_1} e^{-\beta \mathcal{H}_N[\sigma]}$$
(2.6)

we have restored the V, N dependence and used the definition of Ω , (2.7). Each term of Z is proportional to the *canonical probability density* of configuration σ :

$$p_{\beta,V,N}(\boldsymbol{\sigma}) = \frac{e^{-\beta \mathcal{H}[\boldsymbol{\sigma}]}}{Z(\beta,V,N)}$$
(2.7)

For large N, the sum on E_1 in 2.6 is dominated by the saddle point contribution (see the footnote 3):

$$Z(\beta, V, N) = e^{-\beta N f(\beta, v)} \qquad \text{large } N$$
(2.8)

where

$$f(\beta, v) = \min \phi(\epsilon, \beta, v) \tag{2.9}$$

$$\phi(\epsilon, \beta, v) = \epsilon - Ts_{\rm m}(\epsilon, v) \tag{2.10}$$

the last quantity being the free energy functional. Reasoning as in the precedent paragraph when we discussed the microcanonical ensemble, one concludes that the function f appearing in 2.9 can be identified with the thermodynamic (per particle) free energy, F/N appearing in 1.3, which is the thermodynamic potential of the T, V, N ensemble:

$$\beta F(\beta, V, N) = -\ln Z(\beta, V, N) \tag{2.11}$$

The minimisation in 2.9 shows that $\beta = \partial_{\epsilon} s_{\rm m}$ or, in other words, the β appearing in 2.9 is the same of the microcanonical ensemble. Since β and f in 2.9 coincide with their respective thermodynamic quantities, we recognize in 2.9 the Legendre transform that links F and S, $f = \epsilon - Ts$, and hence we can identify the thermodynamic function $\epsilon(\beta, v) = \arg \max_{\epsilon'} \phi(\epsilon, \beta, v)$.

Using the relation (2.11), and (1.3), one can relate to Z all the thermodynamic variables as a function of (β, V, N) . We begin by $S = -\partial_T F$. Using 2.11 one obtains $S = -\beta F + \langle \mathcal{H} \rangle_{\beta,V}$, where the average $\langle \cdot \rangle_{\beta,v}$ is with respect to the distribution 2.7. Since F = E - TS, we obtain that $\epsilon(\beta, v) = \langle \mathcal{H} \rangle_{\beta,v}/N$. Summarizing, the thermodynamic variables are obtained from the ensemble averages as:

$$\epsilon(\beta, v) = \arg\max_{\epsilon'} \{\epsilon' - (1/\beta)s_{\mathrm{m}}(\epsilon')\} = \langle \mathcal{H} \rangle_{\beta, v} / N$$
(2.12)

$$s(\beta, v) = s_{\rm m}(\epsilon(\beta, v)) \tag{2.13}$$

The (per-particle) specific heat $c(\beta, v) = -\beta^2 \partial_\beta \epsilon(\beta, v)$ turns out to be (check it!)

$$c(\beta, v) = \beta^2 N^{1/2} [\langle \epsilon^2 \rangle_{\beta, v} - \langle \epsilon \rangle_{\beta, v}^2]$$
(2.14)

from which one learns that the fluctuations of the energy per site decreases as $N^{-1/2}$ (since the left-hand side is intensive, i.e., of order zero in N). This also happens (check it!) with fluctuations in v.

Isothermal-isobaric ensemble. Proceeding as in the two precedent paragraphs, consider the system divided into two subsystems whose (intensive) volumes assume the values v_1 , $v - v_1 \gg v_1$, respectively. Proceeding as before, the canonical partition function of the composite system results to be:

$$Z(\beta, V, N) = Z_1(\beta, V_1, N_1) \Theta(\beta, P, N_1)$$

$$(2.15)$$

where Θ is the partition function of the isothermal-isobaric ensemble:

$$\Theta(\beta, P, N) = \int dv \, Z(\beta, Nv, N) e^{-\beta N P v}$$
(2.16)

in the large-N limit, it is

$$\Theta(\beta, P, N) = e^{-\beta N g(\beta, P)} \qquad \text{large } N \tag{2.17}$$

where

$$g(\beta, P) = \min_{v} [f(\beta, v) + Pv]$$
(2.18)

such a minimization remember us that $P = -\partial_v F$, and consequently that g is indeed the (intensive) Gibbs potential G/N:

$$-\beta G(\beta, P, N) = \ln \Theta(\beta, P, N)$$
(2.19)

If one knows the function Θ , using the relation (2.19) and the thermodynamic relations (1.3), one can compute the expectation value of thermodynamic quantities.

Equivalence of ensembles. In the T, V ensemble one can compute $P(T, V) = -\partial_V F$, and in the T, P ensemble, one can compute $V(T, P) = -\partial_P G$, where G(T, P) = F + PV, and P(T, V) is indeed the inverse function of V(T, P) at constant temperature. Under suitable conditions to be met by the interaction, and in the limit of large N, the equivalence holds also in statistical physics: if one manages to calculate F as $\beta F = -\ln Z$ and G as $\beta G = -\ln \Theta$, then G is the Legendre transform of F, G = F + PV, and the resulting thermodynamic relations (say, P(T, V) and V(T, P)) are equivalent. One can, hence, choose the most suitable ensemble in the ensemble calculation.