1   Introduction

A general theorem is formulated; a simple case is treated in detail; basic physical notions are tentatively introduced for this case.

1a   Ideal systems of statistical physics

In classical mechanics, the state of a particle may be described by the coordinate $x \in \mathbb{R}^3$ and the momentum[1] $p \in \mathbb{R}^3$. These states form the phase space $\mathbb{R}^3 \times \mathbb{R}^3$, endowed with the Lebesgue measure. More general state spaces are used; each one is endowed with a measure.[2] The measure of the whole phase space may be finite or infinite.

Spin systems do not fit into classical mechanics, but still, classical statistical physics treats also classical spins. For a spin, the phase space is a finite set endowed with the counting measure.

For our purposes, a phase space consists of a set Ω and a σ-finite (positive) measure μ on Ω (on a given σ-field); $\mu(\Omega) \in (0, \infty]$.[3]

Given two systems described by (Ω_1, μ_1) and (Ω_2, μ_2), the combined system is described by the product space $(\Omega_1 \times \Omega_2, \mu_1 \times \mu_2)$.

In classical mechanics, the energy is a smooth function (Hamilton function, or Hamiltonian) on the phase space.[4]

For our purposes, a Hamiltonian is a measurable function $h : \Omega \to \mathbb{R}$.

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[1]In fact, $p = m\dot{x}$, but we do not need it.

[2]In fact, endowed with a symplectic form and therefore a measure. For now, we do not need the symplectic form.

[3]If you are not acquainted with measure theory, you may take just an interval (bounded or unbounded) with Lebesgue measure; it is all the same for the general theory.

[4]Together with the symplectic form it generates the dynamics. For now we do not need the dynamics.

For two *noninteracting* systems with Hamiltonians $h_1 : \Omega_1 \to \mathbb{R}$, $h_2 : \Omega_2 \to \mathbb{R}$, the Hamiltonian of the combined system is $h_1 \oplus h_2 : \Omega_1 \times \Omega_2 \to \mathbb{R}$, $(h_1 \oplus h_2)(\omega_1, \omega_2) = h_1(\omega_1) + h_2(\omega_2)$.

In statistical physics, an *ideal* system consists, by definition, of many noninteracting particles.[1]

In order to describe ideal systems we define

$$\Omega^n = \underbrace{\Omega \times \cdots \times \Omega}_{n}; \quad h^{(n)} : \Omega^n \to \mathbb{R},$$

$$h^{(n)}(\omega_1, \ldots, \omega_n) = \frac{1}{n}\big(h(\omega_1) + \cdots + h(\omega_n)\big).$$

For simplicity, all the particles are assumed to have the same one-particle Hamiltonian h. The Hamiltonian of the system is $nh^{(n)}$. Note the linearity:

$$(ch)^{(n)} = ch^{(n)} \quad \text{and} \quad (f+g)^{(n)} = f^{(n)} + g^{(n)}.$$

Physically, functions of the form $f^{(n)}$ are *macroscopic* observables.[2]

All non-pathological Hamiltonians of statistical physics satisfy one of the following two conditions:

(1a1) $\mu(\Omega) < \infty$ and $\forall \lambda \in (-\infty, +\infty)$ $\displaystyle\int_\Omega \exp(\lambda h)\, \mathrm{d}\mu < \infty$;

(1a2) $\mu(\Omega) = \infty$ and $\forall \lambda \in (-\infty, 0)$ $\displaystyle\int_\Omega \exp(\lambda h)\, \mathrm{d}\mu < \infty$.

1a3 Exercise. Prove that $(\Omega^n, h^{(n)})$ satisfies (1a1) if and only if (Ω, h) does; and the same for (1a2).

1b Concentration of conditional measure

1b1 Definition. Given measurable sets $A, B \subset \Omega$ such that $0 < \mu(A) < \infty$, we define the *conditional probability*

$$\mathbb{P}\big(B\,\big|\,A\big) = \frac{\mu(A \cap B)}{\mu(A)}.$$

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[1] "The importance of these systems lies first in their simplicity. ... ideal systems do not exist in nature. There is even a fundamental inconsistency in taking this concept too seriously." R. Balescu, "Equilibrium and nonequilibrium statistical mechanics", 1975, Sect. 5.1 "Definition of ideal systems".

[2] This is the simplest form of a macroscopic observable.

The same holds for $A, B \subset \Omega^n$.

By $\mathbb{P}\big(g^{(n)} \in J \,\big|\, f^{(n)} \in I\big)$ we mean $\mathbb{P}\big(B\,\big|\,A\big)$ where $A = \{\omega \in \Omega^n : f^{(n)}(\omega) \in I\}$ and $B = \{\omega \in \Omega^n : g^{(n)}(\omega) \in J\}$.

Recall that $\operatorname{ess\,sup} f$ is the least x such that $f(\cdot) \leq x$ almost everywhere; $\operatorname{ess\,inf} f$ is defined similarly; $-\infty \leq \operatorname{ess\,inf} f \leq \operatorname{ess\,sup} f \leq +\infty$. The equality $\operatorname{ess\,inf} f = \operatorname{ess\,sup} f$ means that $f = \text{const}$ almost everywhere (I'll often omit this "almost everywhere").

1b2 Definition. Let $f, g : \Omega \to \mathbb{R}$ be measurable, $f \neq \text{const}$, and $\varphi : (\operatorname{ess\,inf} f, \operatorname{ess\,sup} f) \to \mathbb{R}$ continuous. We write

$$[g|f] = \varphi$$

if the following conditional probability is well-defined for large n and converges to 1:

$$\mathbb{P}\big(g^{(n)} \in (c, d) \,\big|\, f^{(n)} \in [a, b]\big) \to 1 \quad \text{as } n \to \infty$$

whenever $[a, b] \subset (\operatorname{ess\,inf} f, \operatorname{ess\,sup} f)$ and $(c, d) \subset \mathbb{R}$ satisfy $\varphi\big([a, b]\big) \subset (c, d)$.

Roughly, $[g|f] = \varphi$ means that conditionally, given $f^{(n)}$, we have $g^{(n)} \approx \varphi\big(f^{(n)}\big)$ for large n, with high probability.

1b3 Exercise. If $[g|f] = \varphi_1$ and $[g|f] = \varphi_2$ then $\varphi_1 = \varphi_2$.
Prove it.

1b4 Theorem. Let measurable $f, g : \Omega \to \mathbb{R}$ be such that for some $\varepsilon > 0$ the two functions $f \pm \varepsilon g$ satisfy (1a1) or (1a2), and $f \neq \text{const}$. Then $[g|f] = \varphi$ for some continuous $\varphi : (\operatorname{ess\,inf} f, \operatorname{ess\,sup} f) \to \mathbb{R}$.

We'll prove it, but much later.

1c   A simple example

Let Ω be $\mathbb{R}^2$ and μ be the two-dimensional standard normal distribution,

$$\mu = \gamma^2, \quad \gamma^2(A) = \int_A \frac{1}{2\pi} \mathrm{e}^{-|\omega|^2/2} \, \mathrm{d}\omega \, .$$

We restrict ourselves to *linear* Hamiltonians,

$$f(\omega) = \langle f, \omega \rangle, \quad f \in \mathbb{R}^2 \, .$$

They satisfy (1a1) (think, why).

For now we choose this example only for its mathematical simplicity. Later (in Sect. 3a) we'll see that it can approximate spin systems at high temperatures.

Our μ being a probability measure, μ-measurable functions may be treated as random variables. Well-known properties of the normal distribution ensure that $(\omega_1 + \cdots + \omega_n)/n$ is distributed like $\omega_1/\sqrt{n}$, therefore, concentrated near the origin. Moreover, its conditional density on the line

$$f^{(n)}(\omega) = \left\langle f, \frac{\omega_1 + \cdots + \omega_n}{n} \right\rangle = a$$

is concentrated near the closest to the origin point of this line, $S_{f,a} = af/\|f\|^2$. At this point, the value of another linear function g is $g(S_{f,a}) = a\frac{\langle f,g \rangle}{\|f\|^2}$. Thus we guess that $[g|f] = \left(a \mapsto a\frac{\langle f,g \rangle}{\|f\|^2}\right)$, or simply,

(1c1) $$[g|f] = \frac{\langle f, g \rangle}{\|f\|^2} \,.$$

1c2 Exercise. Prove (1c1) without using Theorem 1b4.

Conditionally, given $f^{(n)} \approx a$, we have[1] $g^{(n)} \approx [g|f]a = \frac{\langle f,g \rangle}{\|f\|^2}a = \langle g, S_{f,a} \rangle$. In that sense $S_{f,a}$ is a *macroscopic state* of the physical system; it determines the values of all macroscopic observables.

Physically, $S_{f,a}$ is the *equilibrium state* of the system with Hamiltonian f and the energy per particle a (that is, total energy na). Other points of the line $f(\cdot) = a$ are non-equilibrium states (for the same f and a).

1d   Relaxation to equilibrium

Is it feasible, to get a physical system in a non-equilibrium state? Yes, easily. We take a system in the equilibrium state $S_{f,a}$ and suddenly change its Hamiltonian from f to g (which means physically, a mechanical influence). At first, the state remains $S_{f,a}$ and the energy jumps from $a = \langle f, S_{f,a} \rangle$ to $b = \langle g, S_{f,a} \rangle$. Then the non-equilibrium state changes gradually towards $S_{g,b}$ (the energy being constant) and after a time it becomes practically equal to $S_{g,b}$; an equilibrium again. This process is called *relaxation.*

Unfortunately, it is very difficult to give a (microscopical) model of relaxation that is both rigorous mathematically and realistic physically. For now we just postulate that the system relaxes from $S_{f,a}$ to $S_{g,b}$.

In terms of relaxation it is easy to understand what is wrong in the following naive argument. If $f^{(n)} \approx a$ then $g^{(n)} \approx b$ where $b = [g|f]a$.

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[1]For large n, with high probability, as before...

Similarly, if $g^{(n)} \approx b$ then $h^{(n)} \approx c$ where $c = [h|g]b$. Thus, if $f^{(n)} \approx a$ then $h^{(n)} \approx c$, and therefore $[h|g][g|f] = [h|f]$ (*wrong!*).

Relaxation is irreversible in the following sense: if $a_{k+1} = \langle h_{k+1}, S_{h_k, a_k} \rangle$ for $k = 0, \ldots, n-1$ then $S_{h_n, a_n} \neq S_{h_0, a_0}$ unless $h_0 = h_1 = \cdots = h_n$. Proof: $\|S_{h_{k+1}, a_{k+1}}\| < \|S_{h_k, a_k}\|$ unless $h_{k+1} = h_k$.

1e   Heat transfer; equal temperatures

The same space $(\mathbb{R}^2, \gamma^2)^n$ may be treated as $(\mathbb{R}^1, \gamma^1)^n \times (\mathbb{R}^1, \gamma^1)^n$; a combined system, of two subsystems, each containing n one-dimensional particles. We have (check it) $h^{(n)} = f^{(n)} \oplus g^{(n)}$ whenever $f, g \in \mathbb{R}$, $h = f \oplus g \in \mathbb{R}^2$. Thus, $h^{(n)}$ describes two *noninteracting* systems with Hamiltonians $nf^{(n)}$ and $ng^{(n)}$.

An equilibrium state $S_{h,a}$ of the combined system determines the values of all macroscopic observables of the combined system, and in particular, of each subsystem separately:

$$S_{h,a} = (x, y); \quad \langle f \oplus 0, S_{h,a} \rangle = \langle f, x \rangle; \quad \langle 0 \oplus g, S_{h,a} \rangle = \langle g, y \rangle;$$

the first subsystem is in the macroscopic state x, the second — y. In dimension one $\langle f, x \rangle$ is just fx. The energy decomposes:

$$\underbrace{\langle h, S_{h,a} \rangle}_{a} = \underbrace{\langle f, x \rangle}_{b} + \underbrace{\langle g, y \rangle}_{c}; \quad x = S_{f,b}, \ y = S_{g,c}$$

(check it); we assume $f \neq 0$, $g \neq 0$.

Other decompositions, $a = b' + c'$, of the same a, correspond to nonequilibrium states (of the combined system) with the same energy.

Thus, relaxation of the combined system means redistribution of the given energy between the two subsystems.

A paradox: energy exchange between noninteracting subsystems![1]   In fact, they are only approximately noninteracting. An interaction term in the Hamiltonian is relatively small, and the relaxation time is large (on the microscopic scale).

The equilibrium decomposition $a = b + c$ minimizes $x^2 + y^2 = \left(\frac{b}{f}\right)^2 + \left(\frac{c}{g}\right)^2$; differentiation gives $\frac{b}{f^2} = \frac{c}{g^2}$. Physically it means equal temperatures. We see that the temperature of the first subsystem should be some function[2] of $b/f^2 = x/f$.

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[1] Recall footnote 1 on page 2.

[2] In fact, the temperature is $-\frac{1}{k_B} \frac{f^2}{b}$, where $k_B = 1.38 \cdot 10^{-23}$ J/K is the so-called Boltzmann constant. In this model zero energy corresponds to infinite temperature, and negative energy — to finite positive temperature.

1f   Mechanical energy and thermal energy

The one-dimensional model $(\mathbb{R}^1, \gamma^1)^n$ is especially simple: no relaxation, all states are equilibrium states, just because for given f and a there exists only one x satisfying $\langle f, x \rangle = a$.

A mechanical influence on the system (recall Sect. 1d) is described by switching its Hamiltonian from f to g without changing the state x. The energy jumps from $a = \langle f, x \rangle$ to $b = \langle g, x \rangle$. No relaxation: $S_{f,a} = x = S_{g,b}$.

A thermal influence on the system (as in Sect. 1e) is described by changing its energy from a to b without changing the Hamiltonian f; the state changes from x to y; $a = \langle f, x \rangle$, $b = \langle f, y \rangle$; $x = S_{f,a}$, $y = S_{f,b}$.[1]

On the plane (f, x) a mechanical influence changes only the first coordinate, a thermal influence — only the second. The energy, being a function $(f, x) \mapsto \langle f, x \rangle = fx$ on the plane, changes in both cases; it is energy exchange between the system and its environment. In the former case it is exchange of mechanical energy, in the latter case — thermal energy.

Consider a loop of four changes:

	(f_1, x_1)	$\mapsto$	(f_2, x_1)	$\mapsto$	(f_2, x_2)	$\mapsto$	(f_1, x_2)	$\mapsto$	(f_1, x_1)
total energy	$f_1 x_1$		$f_2 x_1$		$f_2 x_2$		$f_1 x_2$		$f_1 x_1$
increase of total energy		$x_1 \Delta f$		$f_2 \Delta x$		$-x_2 \Delta f$		$-f_1 \Delta x$	
increase of mech. energy		$x_1 \Delta f$		0		$-x_2 \Delta f$		0	
increase of therm. energy		0		$f_2 \Delta x$		0		$-f_1 \Delta x$	

The net result: the system receives from the environment mechanical energy $x_1 \Delta f - x_2 \Delta f = -\Delta f \Delta x$ and thermal energy $f_2 \Delta x - f_1 \Delta x = \Delta f \Delta x$.

An important implication: we cannot split the energy of a system into mechanical part and thermal part. Rather, we can split energy exchange into mechanical (work) and thermal (heat flow).

An even more important implication: an engine can transform repeatedly heat flow into work, or work into heat flow.

1g   Processes and cycles: quasistatic, adiabatic, isothermal

We return to the space $(\mathbb{R}^2, \gamma^2)^n$, be it one system of two-dimensional particles or two systems of one-dimensional particles. Relaxation is irreversible (recall Sect. 1d), but the irreversibility can be made arbitrarily small. For example, consider $h_k = (\cos \varepsilon k, \sin \varepsilon k) \in \mathbb{R}^2$ and $a_0 = 1$. We have $S_{h_0, a_0} =$

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[1]Such influence is implemented via relaxation of a larger system.

$x_0 = (1,0)$ and $a_1 = \langle h_1, x_0 \rangle = \cos \varepsilon$; $S_{h_1,a_1} = x_1 = \cos \varepsilon \cdot (\cos \varepsilon, \sin \varepsilon)$, the orthogonal projection of x_0 to the direction of h_1. Similarly, x_2 is the projection of x_1 to the direction of h_2, and so on;

$$x_k = \cos^k \varepsilon \cdot (\cos \varepsilon k, \sin \varepsilon k) \, ; \quad \|x_k\| = \cos^k \varepsilon \, .$$

For a fixed ε, $x_k \to 0$ as $k \to \infty$. However, consider the limit as $k \to \infty$, $\varepsilon_k \to 0$, $\varepsilon_k k \to t$. We have $\cos^k \varepsilon_k = \left(1 + O\left(\frac{1}{k^2}\right)\right)^k \to 1$, thus $x_k \to (\cos t, \sin t)$, $\|x_k\| \to 1$. In the limit, the point moves along the unit circle, and will return to the initial point.

If we influence the system (mechanically or/and thermally) very slowly, then the system remains all the time in a nearly equilibrium state. In other words: if relaxation is fast enough (on our macroscopic time scale) we may ignore it, assuming that the state of the system is continuously changing in time, but remains an equilibrium state at all times.

Mathematically we may define a *quasistatic process* as a pair of functions, $t \mapsto h_t$ and $t \mapsto a_t$, from $[0,1]$ (or some $[0, t_{\max}]$) to $\mathbb{R}^2$; the functions will be assumed piecewise smooth. We define one more function $t \mapsto x_t \in \mathbb{R}^2$ by $x_t = S_{h_t,a_t} = a_t h_t / \|h_t\|^2$, the equilibrium state corresponding to the Hamiltonian h_t and the energy (per particle) a_t. Thus, $a_t = \langle h_t, x_t \rangle$. Finally, we split the energy received by the system,[1]

$$a_1 - a_0 = \langle h_1, x_1 \rangle - \langle h_0, x_0 \rangle = \int_0^1 \left(\langle h_t', x_t \rangle + \langle h_t, x_t' \rangle \right) \mathrm{d}t$$

into the *mechanical* part defined by

$$\int_0^1 \langle h_t', x_t \rangle \, \mathrm{d}t \, ,$$

and the *thermal* part defined by

$$\int_0^1 \langle h_t, x_t' \rangle \, \mathrm{d}t \, .$$

The reason should be clear from Sect. 1f. Infinitesimally, a mechanical influence corresponds to the transition from (h, x) to $(h + \mathrm{d}h, x)$ (with subsequent relaxation not changing energy), while a thermal influence — from (h, x) to $(h, x + \mathrm{d}x)$. And do not forget that h_t and x_t stay collinear.

1g1 Exercise. Check that

$$\langle h_t', x_t \rangle = (\operatorname{sgn} a_t) \|x_t\| \frac{\mathrm{d}}{\mathrm{d}t} \|h_t\| \, ,$$

$$\langle h_t, x_t' \rangle = (\operatorname{sgn} a_t) \|h_t\| \frac{\mathrm{d}}{\mathrm{d}t} \|x_t\| \, .$$

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[1]Of course, z' denotes here the time derivative of z.

A quasistatic process is called a (thermodynamic) *cycle,* if $h_0 = h_1$ and $a_0 = a_1$. For a quasistatic cycle, the total energy received by the system vanishes.

A quasistatic process is called *adiabatic,*[1] if

$$\langle h_t, x'_t \rangle = 0 \quad \text{for all } t.$$

This is the case when the system is perfectly insulated thermally. An equivalent condition: $\|x_t\| = \text{const}$. We see that some function of x_t is preserved by all adiabatic processes. Later we'll see that this is a property of *thermodynamic entropy*, closely related to probabilistic entropy. Thus, entropy is some function[2] of $\|x\|$.

All said holds also for $(\mathbb{R}^1, \gamma^1)^n$, in which case, for a quasistatic cycle, both mechanical and thermal energy is (up to a sign) just the area inside the closed curve on the (f, x) plane, provided that the curve does not intersect itself. The area may be used for $(\mathbb{R}^2, \gamma^2)^n$, in which case we consider the pair $(\|h_t\|, \|x_t\|)$ as a point on a plane (and do not forget $\text{sgn}\, a_t$).

For $(\mathbb{R}^1, \gamma^1)^n$ the temperature is a function of $a/\|h\|^2$, recall Sect. 1e. It is easy to see that the same holds for $(\mathbb{R}^2, \gamma^2)^n$. Thus, a quasistatic process is called *isothermal,* if

$$\frac{a_t}{\|h_t\|^2} = \text{const}.$$

Equivalently, $x_t = \text{const} \cdot h_t$. This typically occurs when a system is in contact with an outside thermal reservoir (heat bath), and the change occurs slowly enough to allow the system to continually adjust to the temperature of the reservoir through heat exchange.[3]

1g2 Exercise. For an isothermal quasistatic cycle, the mechanical energy received by the system vanishes; the same holds for the thermal energy.

Check it.[4]

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[1] Also "isocaloric". The term "adiabatic" is used differently outside thermodynamics.

[2] In fact, the thermodynamic entropy per particle is $-\frac{1}{2} k_{\text{B}} \|x\|^2$.

[3] This phrase is copied from Wikipedia.

[4] The result holds far beyond our special case. Probably you derive it by integrating differential relations specific to this case. Maybe you find them strange, if you compare them with something like a gas in a cylinder with a piston. If puzzled, try a vertical cylinder with a heavy piston. . .

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