Statistical mechanics of entropic forces: disassembling a toy

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Abstract

The notion of entropic forces often stays mysterious to students, especially to ones coming from outside physics. Although thermodynamics works perfectly in all cases when the notion of entropic force is used, no effort is typically made to explain the mechanical nature of the forces. In this paper we discuss the nature of entropic forces as conditional means of constraint forces in systems where interactions are taken into account as mechanical constraints and discuss several examples of such forces. We moreover demonstrate how these forces appear within the standard formalism of statistical thermodynamics and within the mechanical approach based on the Pope–Ching equation, making evident their connection with the equipartition of energy. The paper is aimed at undergraduate and graduate students studying statistical physics and the teachers teaching it.

1. Motivation

The idea of this text emerged after several years of teaching polymer physics to engineers and chemists, which led me to the necessity to develop a transparent and conceptually easy course accessible to a rather heterogeneous audience. After some less successful attempts, the course was polished enough to run smoothly, i.e. without getting confronted with 'stupid questions', and with good average marks at the final examination.

The standard introductory course in polymers begins as follows. One starts from discussing some aspects of chemistry and getting rid of unnecessary details, coming to a simple model of a polymer as a freely jointed chain and then as a random walk chain. Then one considers the combinatorial problem of calculating the number of possible conformations W of a chain under different constraints, for example $W(x)$ with x being the fixed end-to-end distance. One then calculates the conditional entropy by taking $S(x) = k_B \ln W(x)$, where k_B is the Boltzmann constant, and then thermodynamics starts. Neglecting all interactions except for those which keep the chain together (and are represented by mechanical constraints) one

argues that the internal energy of the chain does not depend on its conformation, $U = \text{const}$, so that its free energy

$$F(x) = U - TS(x) \tag{1}$$

depends on coordinates only through the entropic term, and then

$$f(x) = -\frac{\mathrm{d}F}{\mathrm{d}x} = T\frac{\mathrm{d}S}{\mathrm{d}x}. \tag{2}$$

Since the overall number of conformations $W(x)$ corresponding to the fixed coordinate x is connected to the probability $p(x)$ of finding the end of a free chain at a position x, $p(x) = W(x)/W = C^{-N}W(x)$, where W is the overall number of different conformations of a chain with N bonds, being equal to C^N for a random walk chain on a lattice with coordination number C, we have

$$f(x) = k_B T \frac{\mathrm{d}}{\mathrm{d}x} \ln p(x), \tag{3}$$

and the problem of finding the force is solved as soon as $p(x)$ (being a Gaussian in a random walk model with $N \gg 1$) is known.

However, once a question came: 'And where does the force come from?' To avoid the question, one can discuss immediately other examples of similar forces, like the pressure of the ideal gas, to show that the concept works universally. This is exactly what is done in the brilliant Grosberg and Khokhlov's book [1]. This concept paid off: I never got the question again.

Another time a question came: 'And can one do all this without entropy?' The answer was: 'Yes, I can, but this will be much more complicated'. To avoid this one, I start with asking, whether everybody is familiar with the notions of entropy and of free energy, and only then start with the calculations. The question came never again. However, the students were right; the thermodynamical approach is somewhat like a Chinese cylinder trick: you put a dove in, and the rabbit comes out, and it is not clear what happens in between.

Moreover, to baffle the audience, one often introduces the notion of the 'entropic force'. For example, since the internal energy of an ideal gas does not depend on its volume (but only on temperature and the number of particles), the free energy $F = U - TS$ depends on the volume only via entropy S. A characteristic property of entropic forces is the fact that they are proportional to $k_B T$ as the pressure of ideal gas or elastic force of a polymer molecule. Once, at a conference, I decided to use the question on the nature of the force, and put it to a younger colleague: 'And where does the force come from?' The answer was: 'It is purely entropic!'

Since neither temperature nor entropy is a 'mechanical quantity', one can conclude that there exists some 'non-mechanical force'. Or what? Interestingly enough, none of my clever students ever asked the question on this 'non-mechanical force', so I had to put it myself.

2. Calculating pressure

We start from considering several examples which elucidate the notions in more and more detail, and then discuss its deep rooting in classical statistical mechanics and its connection with equipartition of energy.

First, let us calculate the pressure which an ideal gas exerts on a solid wall. We know a mechanistic explanation, which essentially stems from Bernoulli and is perfectly good for gases. We namely know that the pressure can be expressed through the total momentum change of the molecules hitting the wall per unit time within unit square of its surface. The mechanical part here is clear: force is momentum change per unit time. This explanation and

the corresponding calculation are given in a beginner's course in physics (see e.g. [2] or [3]). However, this is not the way we calculate pressure in statistical thermodynamics.

Since we are interested in a fixed-temperature setup (we want to know p as a function of T and V) we use the canonical ensemble. We first calculate the partition function $Z(N, V, T)$ (see e.g. [4]) and note that the kinetic part, the one depending on velocities, factorizes! Since it does not depend on volume, we can immediately consider it as a multiplicative constant, depending only on temperature and on the number of particles:

$$Z(N, V, T) = C(N, T)Q(N, V, T),\qquad(4)$$

where $Q(N, V, T)$ is called a configuration integral. Whatever assumptions about the particles (distinguishable, indistinguishable, mixture of particles of different sorts), the configuration integral is proportional to V^N, so that the overall structure of Q is

$$Q(N, V, T) = C_1(N, T)V^N.\qquad(5)$$

Then we use the connection of Z with free energy

$$F = -k_B T \ln Z = -k_B T N \ln V + \text{const},\qquad(6)$$

where the constant $= -k_B T(\ln C_1(N, T) + \ln C(N, T))$ depends on N and T, but not on V, and apply the thermodynamical relation $p = -\partial F/\partial V$ to obtain

$$p = k_B T N/V.\qquad(7)$$

Now, the rabbit is here, in a kind of magic trick. The magic part is as follows: all kinetic properties, which were contained in the constant, were removed after differentiation, and therefore seem to play no role. The question, however, stays: Where does the force come from?

3. Statistical physics: thermodynamics versus mechanics

The difficulties with understanding the nature of entropic forces arise from the fact that in teaching statistical physics one relies on the concepts of thermodynamics, i.e. on the interpretation of the statistical entropy as thermodynamic entropy, and does not discuss the mechanical nature of these forces. This approach works perfectly well, but does not answer the question posed above.

A brief analysis shows that the notion of an entropic force is invoked in situations where interactions in a system are modelled by mechanical constraints: in the cases which appear as examples, the internal energy of the system (being the mean of its Hamilton function) is independent of the configuration, and therefore the free energy

$$F = U - TS\qquad(8)$$

depends on the external variables only via entropy. The most prominent examples of such systems are the polymer molecule, the ideal gas and colloidal systems.

The systems in which interactions are modelled via mechanical constraints are popular models in theoretical physics of polymers and colloids, and are often called 'athermal' (or 'athermic') in the slang of these disciplines. The so-called entropic forces appearing in the description of such systems are the statistical mechanics counterparts of the reaction forces representing mechanical constraints in dynamics (i.e. the reaction forces of the walls of the vessel containing a gas, the forces keeping a polymer molecule together, etc). These are purely mechanical forces (as always in macroscopic physics, essentially of electromagnetic nature), which do not have to be calculated explicitly, so their nature does not play a role in the answer. A missing link (which explains what happens between the beginning and the end of the trick,

i.e. between putting dove in and the rabbit coming out) is connected with the notion of the *mean force*. The aim of this text is to disassemble the toy and to elucidate the trick, namely to show its connection with the basic concepts of classical statistical mechanics. The word 'classical' here means that quantum effects can be neglected, and the equipartition theorem holds. In what follows we proceed to show how entropic forces appear as conditional averages of the reaction forces due to constraints, a twist, which, to my best knowledge, was never discussed in detail before in a pedagogical manner.

The plan of our further considerations is as follows:

We first discuss the simplest example of entropic forces: the pressure of ideal gas, and show how the entropic forces appear when averaging the reaction forces over the corresponding Gibbs–Boltzmann distributions. We note that the derivation of the Gibbs–Boltzmann distribution (at least within the Jaynes' approach to statistical physics [5]) does not rely on thermodynamical interpretation of entropy, so that we stay in the framework of statistical physics and classical mechanics, which will be our aim throughout the paper.

We then consider the problem of calculating the pressure in a gas of interacting particles, to show how the standard thermodynamical approach is connected with the previous one.

Afterwards we discuss the notion of the mean force (and illustrate it by calculating the tension of a polymer molecule and by the Fick–Jacobs setup) and finally show that purely mechanical considerations, augmented by the notions of equilibrium and equipartition, lead to these well-known results, which are thus fundamental, and not merely a coincidence.

4. Pressure of an ideal gas: a statistical mechanics approach

In the previous section we used the thermodynamical relation, because we associated informational entropy of statistical physics with thermodynamical entropy. However, we do not need thermodynamics at all, and can stay within the statistical theory of Gibbs ensembles. It is interesting to see how it works for an ideal gas, since this knowledge will help us to understand some peculiarities of entropic forces as appearing in other situations, such as colloids and polymers.

In order to do so, we first have to dispense from considering the wall as a pure boundary condition, since the potential at the wall has to diverge, and we do not yet know how to average infinity over any distribution. In a kinetic description this is circumvented by considering momentum well before and well after the interaction with the wall and relying on the moment conservation. Here we do not have this possibility, but can do the following. Let us consider a rectangular cylinder of length X (with a stiff wall at $-X$ and another wall at 0) of cross-sectional area A (with volume $V = AX$) and calculate the overall force acting on its right wall (the one at 0, see figure 1). Let us imagine any form of the interaction potential between the particles and the wall $U(x)$, about which initially only two things are assumed: $U(x) = 0$ for $x < 0$ where the wall starts and $U(x) \rightarrow \infty$ for $x \rightarrow \infty$ to prevent particles passing through it. However, to be concrete, we can assume the following potential:

$$U(x) = \frac{\kappa}{2}x^2 \tag{9}$$

for $x > 0$ and zero otherwise up to the left wall. Here κ is the stiffness parameter of the wall.

Let us now calculate the mean force acting on this right wall. Since the particles in an ideal gas are non-interacting, it is first enough to concentrate on exactly one particle, essentially
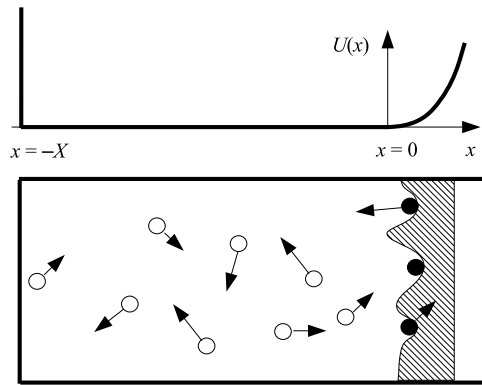
Figure 1. Pressure of the ideal gas. The right wall of the cylinder is considered 'soft', and the force on it is exerted by molecules which actually interact with the wall (shown black). The potential of this interaction force is shown above the sketch.

only on its x-coordinate. The probability of finding a particle at a position x follows from the Boltzmann–Gibbs statistics and is given by

$$p(x) = \text{const} \cdot \exp\left(-\frac{U(x)}{k_B T}\right), \tag{10}$$

i.e.

$$p(x) = C \tag{11}$$

for $-X < x < 0$ and

$$p(x) = C \cdot \exp\left(-\frac{\kappa x^2}{2k_B T}\right) \tag{12}$$

for $x > 0$, where the factor C follows from normalization. We can even calculate this constant: it is

$$C = \left[X + \sqrt{\frac{\pi k_B T}{2\kappa}}\right]^{-1}. \tag{13}$$

For $X \gg \sqrt{k_B T/\kappa}$ (when the overall probability of being within the wall becomes negligible compared to the probability of being outside), the constant C is essentially $C = 1/X$, and the probability of finding the particle at some $x > 0$ is

$$p(x) = \frac{1}{X} \exp\left(-\frac{\kappa x^2}{2k_B T}\right). \tag{14}$$

If we are interested in the probability of finding a particle at some $x > X$ and at some particular values of y and z, we only have to divide this result by the area $A = YZ$ of the wall and obtain

$$p(x, y, z) = \frac{1}{XA} \exp\left(-\frac{\kappa x^2}{2k_B T}\right) = \frac{1}{V} \exp\left(-\frac{\kappa x^2}{2k_B T}\right). \tag{15}$$

Now we can calculate the mean force acting on the particle when interacting with the wall (i.e. when its coordinate $x > 0$). This force acts in the negative x-direction and equals

$$f_x = \int_X^\infty (-\kappa x) p(x, y, z) \, dx \, dy \, dz = -\frac{1}{X} \int_0^\infty \exp\left(-\frac{\kappa x^2}{2k_B T}\right) \kappa x \, dx$$

$$= -\frac{k_B T}{X}. \tag{16}$$

The integral is trivially taken by partial integration. Note that the form of the interaction potential is essentially not important, since the force acting on a particle is $-\partial U(x)/\partial x$, so that

$$-\frac{1}{X} \int_0^\infty \frac{\mathrm{d}U(x)}{\mathrm{d}x} \exp\left(-\frac{U(x)}{k_B T}\right) \mathrm{d}x = -\frac{k_B T}{X} \int_0^\infty \frac{\mathrm{d}}{\mathrm{d}x} \exp\left(-\frac{U(x)}{k_B T}\right) \mathrm{d}x$$
$$= -\frac{k_B T}{X}. \tag{17}$$

We see that the mean interaction force does not depend on the details of the interaction. Taking the wall as stiff changes the interaction force and the mean number of interacting particles, the ones with $x > 0$ (or the probability of finding a particle within the interaction zone $x > 0$), but their product, the corresponding mean force, stays the same. This is the fact that allows us to make a limiting transition to an infinitely stiff wall and consider the wall as a pure constraint.

The previous equation gives us the mean force acting on one particle from the side of the wall; the force acting on the wall differs from this only in its sign, as following from Newton's third law. If N particles are in play, this overall force is N times larger. To obtain pressure, we simply divide the overall force by A:

$$p = Nk_B T/V. \tag{18}$$

Now we know how the entropy works! The force is perfectly mechanical, and moreover, it only depends on the prefactor of the corresponding probability density. This is how the partition function will enter the game in the following section.

5. Gas of interacting particles: disassembling the partition function

Mathematics is about proofs. Physics is about examples. Nevertheless it is interesting to see how the standard expression for the pressure appears within the mechanical picture discussed above for the ideal gas.

In a general situation we start from the thermodynamical relation

$$p = -\frac{\partial F}{\partial V} \tag{19}$$

and use the statistical definition

$$F = -k_B T \ln Z \tag{20}$$

to obtain

$$p = k_B T \frac{\frac{\partial Z}{\partial V}}{Z}, \tag{21}$$

with $Z = Z(V, N, T)$ being the corresponding partition function, depending on volume, number of particles and the temperature of the system. Now we consider another method, parallel to the one of the previous section, to arrive at the same result.

According to the Boltzmann–Gibbs statistics, the probability density of the particle positions/momenta

$$w(\vec{p}, \vec{q}) = \frac{1}{Z} \exp\left(-\frac{H(\vec{p}, \vec{q})}{kT}\right), \tag{22}$$

with $\vec{p}$ and $\vec{q}$ being the vectors comprising all momenta and all coordinates in the system, H being its Hamilton function,

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + V(\vec{q}), \tag{23}$$

and Z being the corresponding partition function

$$Z = \int d\vec{p}\, d\vec{q} \exp\left(-\frac{H(\vec{p}, \vec{q})}{kT}\right).$$ (24)

These are the general relations, valid for any thermodynamical system.

Now let us now consider a gas of interacting particles within the rectangular cylinder of cross-sectional area A with a solid wall at $-X$ and introduce the soft wall, described in the same way as was done in the previous paragraph, at the coordinate $x = X_w$. The introduction of a new variable X_w is the preparation for a mathematical trick which considerably simplifies calculations, and X_w will be set to zero after these calculations are finished.

The interaction with the wall will be described via the interaction potential

$$U(\vec{q}) = \sum_{i=1}^{N} \kappa \frac{(x_i - X_w)^2}{2} \theta(x_i - X_w)$$ (25)

(where only the x-coordinates of the particles play a role, and $\theta(x)$ is the Heaviside theta-function), which, for the description of such an interaction, has to be added to the Hamilton function,

$$H' = H + U.$$ (26)

The force acting on the wall for given positions of all particles is

$$f(\vec{q}) = -\sum_{i=1}^{N} \frac{\partial U(\vec{q})}{\partial x_i} = -\sum_{i=1}^{N} \kappa(x_i - X_w)\theta(x_i - X_w)$$ (27)

(note that no δ-term corresponding to the differentiation of a θ-function appears, since it is multiplied by zero). The mean force acting on the wall is then

$$f_x = \frac{\int d\vec{p}\, d\vec{q}\left[-\sum_{i=1}^{N} \frac{\partial U(\vec{q})}{\partial x_i}\right] \exp\left[-\frac{H(\vec{p},\vec{q})}{kT}\right] \exp\left[-\frac{U(\vec{q})}{kT}\right]}{\int d\vec{p}\, d\vec{q} \exp\left[-\frac{H(\vec{p},\vec{q})}{kT}\right] \exp\left[-\frac{U(\vec{q})}{kT}\right]}.$$ (28)

The integrals over the components of momenta are trivial; they decouple and lead to the same expressions in the denominator and in the numerator, so that

$$f_x = \frac{\int d\vec{q}\left[-\sum_{i=1}^{N} \frac{\partial U(\vec{q})}{\partial x_i}\right] \exp\left[-\frac{V(\vec{q})}{kT}\right] \exp\left[-\frac{U(\vec{q})}{kT}\right]}{\int d\vec{q} \exp\left[-\frac{V(\vec{q})}{kT}\right] \exp\left[-\frac{U(\vec{q})}{kT}\right]}.$$ (29)

Note that the expression for the force has an alternative representation,

$$f(\vec{q}) = \frac{dU(\vec{q})}{dX_w},$$ (30)

which follows immediately from (25), so that

$$-\sum_{i=1}^{N} \frac{\partial U(\vec{q})}{\partial x_i} \exp\left[-\frac{U(\vec{q})}{kT}\right] = kT \frac{d}{dX_w} \exp\left[-\frac{U(\vec{q})}{kT}\right].$$ (31)

Therefore our expression for f_x reads

$$f_x = kT \frac{\frac{d}{dX_w} \int d\vec{q} \exp\left[-\frac{V(\vec{q})}{kT}\right] \exp\left[-\frac{U(\vec{q})}{kT}\right]}{\int d\vec{q} \exp\left[-\frac{V(\vec{q})}{kT}\right] \exp\left[-\frac{U(\vec{q})}{kT}\right]}.$$ (32)

Note that already at this step we recognize the general thermodynamic relation $f_x = (d/dX_w) \ln Z'$, where Z' is the partition function of a system with the modified Hamilton

function H'. In the next step we will consider the wall as more and more stiff, i.e. go to the limit $\kappa \to \infty$, in which case

$$\exp\left(-\kappa \frac{(x_i - X_w)^2}{2kT} \theta(x_i - X_w)\right) \to \theta(X_w - x_i),$$ (33)

so that the integrals in the numerator and in the denominator correspond to the ones over the volume of the system of size $(X + X_w, Y, Z)$. The rest is to divide both parts of this equation by the wall's area A to obtain the pressure

$$p = kT \frac{\frac{\mathrm{d}}{\mathrm{d}V} \int \mathrm{d}\vec{q} \exp\left[-\frac{V(\vec{q})}{kT}\right]}{\int \mathrm{d}\vec{q} \exp\left[-\frac{V(\vec{q})}{kT}\right]}$$ (34)

(note that $\mathrm{d}V = A \, \mathrm{d}X_w$), and to set X_w to zero to return to the initial system's size. Here we have seen how statistical physics works by itself, without any connection to thermodynamics. Restoring the integrals over momenta (which cancelled) we obtain exactly the general equation (21).

6. Mean force

Let us return to our example of the ideal gas, but introduce now an external potential force, say gravity, acting on particles in the x-direction. Let $U(x)$ be the potential of this force. While in the absence of the force the density of the molecules was homogeneous, the external field makes it coordinate dependent. Again let us consider the one-particle picture, where the Boltzmann–Gibbs statistics gives now the expression

$$p(x) = C \exp\left(-\frac{U(x)}{k_B T}\right)$$ (35)

for the probability density $p(x)$ to find it at position x. Imagine, this probability is measured (e.g. by measuring the density of the gas). If it is known, the potential $U(x)$ can be restored from it by inverting this last expression:

$$U(x) = \mathrm{const} - k_B T \ln p(x).$$ (36)

The constant stemming from normalization plays no role, since the potentials are anyhow defined only up to a constant contribution, and the (classical) observable is essentially the force $f(x) = -\partial U / \partial x$, which is defined uniquely. Note that the force corresponding to $U(x)$ *looks like* an entropic force: it has a factor $k_B T$ in front of something related to the probability and hence to the entropy of the system. However, this is a quite normal, and even potential, mechanical force.

Imagine now, we have a complex system, and have a possibility of measuring $p(x)$ in this one. Using (36) we can get some effective potential $U(x)$, which is often called *the potential of the mean force*, and define the corresponding mean force

$$f(x) = k_B T \frac{\mathrm{d}}{\mathrm{d}x} \ln p(x).$$ (37)

This is exactly how, for example, the elastic force in a polymer molecule pulled at the end is evaluated in elementary polymer physics. In our heuristic discussion we obtained (37) for the ideal gas. Let us postpone the discussion of its universal applicability until section 7 and consider now how this expression for the mean force can be used in different realistic situations in order to show that the results coincide with the ones obtained using alternative approaches.
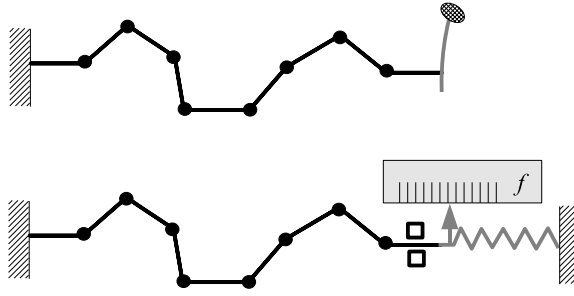
Figure 2. Two situations considered in calculating the tension force of a polymer molecule. The upper picture corresponds to a constrained equilibrium discussed in section 6.1; the end of the chain is fixed by the nail. The lower panel depicts the situation in which the force is actually measured, section 6.2. This situation reduces to the previous one if the spring of the dynamometer gets more and more stiff.

6.1. Tension of a polymer chain I

Typically one considers a grafted chain with one end fixed at the origin and calculates the probability $p(x)$ of finding the other end at position x. The force then follows exactly via (37). The steps of this standard way are as follows.

- Describe your system in Cartesian coordinates, and chose the x-coordinate of the last bead as one of them. The overall set of coordinates will be denoted as $(x, \vec{Q})$ (the last vector does not include x).

  Integration over momenta and all coordinates other than x gives the marginal probability density

$$p(x) = \frac{1}{Z} \int d\vec{p} \int d\vec{Q} \exp\left(-\frac{H(\vec{p}, \vec{Q}, x)}{k_B T}\right), \qquad (38)$$

whose logarithm is the potential of the mean force pertinent to x. Note that the potential of mean force depends on Z only through a non-observable constant term.

  The integral representing the marginal probability density $p(x)$ can be alternatively represented as

$$p(x) = \frac{Z(x)}{Z}, \qquad (39)$$

with $Z(x)$ being the partition function calculated in a system where the coordinate x is fixed (i.e. an additional mechanical constraint is applied, see figure 2, upper panel):

$$Z(y) = \int d\vec{P} \int d\vec{Q} \, dx \exp\left(-\frac{H(\vec{P}, \vec{Q}, x)}{k_B T}\right) \delta(x - y). \qquad (40)$$

The potential of the mean force is therefore

$$U(x) = -k_B T \ln \frac{Z(x)}{Z}, \qquad (41)$$

and the mean force itself reads

$$f(x) = k_B T \frac{\frac{d}{dx} Z(x)}{Z(x)}. \qquad (42)$$

6.2. Tension of a polymer chain II

Here we can also proceed in a 'mechanical' way parallel to the way outlined in section 4. We namely

- model the experimental procedure of measuring the corresponding generalized force by adding a spring at the end of the chain (see figure 2, lower panel), so that

$$H' = H + \frac{\kappa}{2}(x - x_0)^2, \tag{43}$$

  and the partition function corresponding to the Hamilton function H' is Z';
- calculate the mean force via the Boltzmann–Gibbs distribution

$$f_x = \frac{1}{Z'} \int d\vec{p} \int d\vec{Q} \, dx [-\kappa(x - x_0)] \exp\left(-\frac{H(\vec{p}, \vec{Q}, x) + \kappa(x - x_0)^2/2}{k_B T}\right); \tag{44}$$

- take the limit $\kappa \to \infty$ (which corresponds to $\exp(-\kappa(x - x_0)^2/2k_B T) \to \sqrt{2\pi k_B T/\kappa}\delta(x - x_0)$) to get

$$f_x = k_B T \frac{1}{Z'} \int d\vec{p} \int d\vec{Q} \, dx \exp\left(-\frac{H(\vec{p}, \vec{Q}, x)}{k_B T}\right) \frac{d}{dx}\delta(x - x_0), \tag{45}$$

  which, after partial integration, gives us exactly (42),

$$f(x) = k_B T \frac{\frac{d}{dx} Z(x)}{Z(x)}, \tag{46}$$

  since, for $\kappa \to \infty$, Z' tends to the conditional partition function $Z(x)$.

We thus see that (at least for the particular simple example) the concept of the mean force gives us exactly the expression for the force obtained thermodynamically and, on the other hand, correctly describes the force as obtained in an idealized measurement procedure.

6.3. Next step: the Fick–Jacobs setup

Here is yet another example, now less standard and somewhat more interesting, because it unveils some additional features of the mean force approach.

Consider a system of non-interacting particles (say an ideal gas or a dilute solution, where we concentrate on the solute molecules) in a vessel having the form shown in figure 3. The walls put non-holonomic constraints on the particles' motion. We confine ourselves to a two-dimensional setup (generalization to three dimensions is trivial). Let us now assume that the measurement of the one-dimensional density $\rho(x) \propto h(x)$ was performed (e.g. by scattering of light passing through a cross section) and the probability density $p(x)$ is deduced from it by normalization. We now define the potential of mean force

$$U(x) = -k_B T \ln p(x) \tag{47}$$

(omitting the constant contribution) and the mean force

$$f(x) = k_B T \frac{d}{dx} \ln p(x) = k_B T \frac{dh(x)/dx}{h}. \tag{48}$$

This force is an interesting example of entropic forces, and enters immediately as a 'real' driving force if, for example, the diffusion in thin channels with curvilinear walls is considered
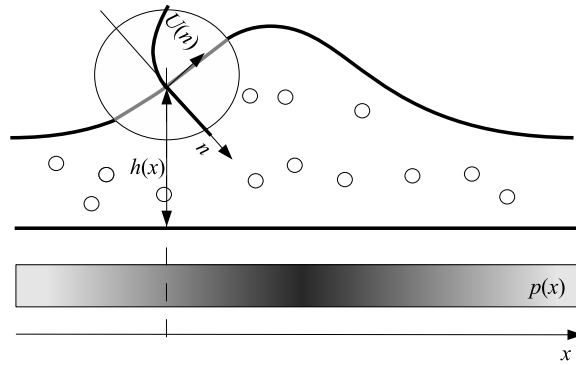
Figure 3. The Fick–Jacobs setup. When considering the projection of the particles' density onto the x-axis (the density is shown on the grey scale at the bottom of the figure) one can argue that there exists an entropic force which acts on the particles and allows them to gather in the middle of the channel where it is broader. The mechanical nature of this force is elucidated in the present section. The potential of the interaction with the wall is depicted in the inset (circle in the upper panel).

(see [6] and [7] for more details). Because of this application to diffusion we call this example the 'Fick–Jacobs setup'. What is the mechanical nature of this entropic force?

Let us fix x and concentrate on the cross section of the vessel by the $x = $ const line. Close to it the upper wall can be considered as flat. It is inclined with respect to the horizontal axis by the angle $\alpha = \arctan(\mathrm{d}h/\mathrm{d}x)$. Let us, like in the previous paragraphs, introduce the interaction potential with the wall, being quadratic in the direction normal to the wall,

$$U(n) = \frac{\kappa}{2} n^2 \tag{49}$$

inside the wall, with n being the coordinate along the normal to the wall taken at the point $(x, h(x))$. When x is fixed, the energy depends only on y-coordinate and is given by

$$U(y) = \frac{\kappa}{2}(y - h)^2 \cos^2 \alpha \tag{50}$$

(with $y \cos \alpha$ being the distance from the point with coordinates (x, y) to the surface of the wall). Let us now concentrate on particles whose coordinate is x, i.e. consider the conditional probability $p(y|x)$. Using the Bayes theorem, this is again given by a Boltzmann expression,

$$p(y) = C \tag{51}$$

for $y < h(x)$ and

$$p(y) = C \exp\left(-\frac{\kappa}{2k_B T}(y - h)^2 \cos^2 \alpha\right) \tag{52}$$

for $y > h(x)$. The constant C can be calculated in the same way as in section 1 and is given by

$$C = \left[h(x) + \sqrt{\frac{\pi k_B T}{2\kappa \cos^2 \alpha}} \right]^{-1}. \tag{53}$$

If the wall is stiff, this constant becomes $C \to 1/h(x)$. The x component of the force acting on the particle is equal to $f_x(y) = 0$ for $y < h(x)$ and is given by the corresponding component

of the elastic force $f_x(y) = \kappa n \sin \alpha = \kappa[y - h(x)] \sin \alpha \cos \alpha$ for $y > h(x)$. Thus, the mean force

$$
\begin{aligned}
f &= C \int_0^\infty f_x(y) p(y) \, \mathrm{d}y \\
&= C \int_{h(x)}^\infty \kappa[y - h(x)] \sin \alpha \cos \alpha \exp\left(-\frac{\kappa}{2k_B T}(y - h)^2 \cos^2 \alpha\right) \\
&= C k_B T \tan \alpha
\end{aligned}
\tag{54}
$$

and is independent of κ (the integral is calculated by the same trick as for the pressure of ideal gas in section 4). Using the expressions for C and α discussed above we get in the limit $\kappa \to \infty$

$$
f(x) = k_B T \frac{\mathrm{d}h(x)/\mathrm{d}x}{h}.
\tag{55}
$$

The mechanical nature of this force is now clear; it is the mean x-component of the reaction force of the wall acting on a particle with a given x-coordinate. In simple words: the mean force is the *conditional average* of the mechanical force acting on the particle (here conditioned on its x-coordinate), i.e a bona fide mean mechanical force. This is essentially a mean constraint force (in our case, a mean force corresponding to a non-holonomic constraint). The statement that the mean force appears as a conditional average is absolutely general, and is intimately connected with the equipartition.

7. Another view on the mean force: the role of equipartition

The notion of the potential of mean force is very deeply rooted in classical statistical physics. In what follows we discuss the situation on a purely mechanical level, and equipartition of kinetic energy is the only thing we need from statistical physics. To see this, we need some additional mathematics, different from the one discussed above. This is given by the Pope–Ching equation, which we will discuss in what follows. This approach is much more transparent than the standard, canonical, one, due to Fixman [8], and works independently of whether the constraints are holonomic or not.

We concentrate at the motion of one particle (or at one generalized coordinate x) and obtain a general relation between the probability density of this coordinate at equilibrium, particle's mean squared velocity and the mean force. This relation is, of course, the same as above; however, some additional insight into the problem can be gained from its consideration from a very different point of view.

Based on purely probabilistic considerations, Pope and Ching [9] derived the equation connecting the probability density of $p(x)$ of a variable x in a stationary state (e.g. in equilibrium) with the mean conditional acceleration $\langle \ddot{x} | x \rangle$ at x and the mean conditional squared velocity at x, $\langle \dot{x}^2 | x \rangle$:

$$
p(x) = \frac{C}{\langle \dot{x}^2 | x \rangle} \exp\left(\int_0^x \frac{\langle \ddot{x} | x' \rangle}{\langle \dot{x}^2 | x' \rangle} \, \mathrm{d}x'\right),
\tag{56}
$$

where the constant C is given by normalization. Contrary to our previous discussion this result holds for any coordinate x (even for a generalized, curvilinear one!).

In Cartesian coordinates this result reduces to the standard canonical one, (37). According to the equipartition theorem, the mean squared velocity of the particle in a canonical ensemble does not depend on its position and is always given by

$$
\langle \dot{x}^2 | x \rangle = v^2 = \frac{k_B T}{m}.
\tag{57}
$$

Therefore,

$$p(x) = C_1 \exp\left(\int_0^x \frac{m\langle \ddot{x}|x\rangle}{k_B T}\right) = C_1 \exp\left(\int_0^x \frac{\bar{f}(x)}{k_B T}\right), \tag{58}$$

with $C_1 = Cm/kT$, where $\bar{f}(x) = \langle f|x\rangle = \langle m\ddot{x}|x\rangle$ is the mean force acting at the particle at position x. Now, taking the logarithm of both parts of the last expression, we see that

$$\ln p(x) = \text{const} + \int_0^x \bar{f}(x')/k_B T \, \mathrm{d}x' \tag{59}$$

and therefore

$$\bar{f}(x) = k_B T \frac{\mathrm{d}}{\mathrm{d}x} \ln p(x). \tag{60}$$

Since here we have to do with an independent, and not well-known, result, a sketch of the derivation of the Pope–Ching equation is given in the appendix. This derivation is even more important in order to show that the connection of the mean force and probability is a theorem of *classical mechanics* and does not rely whatsoever on assumptions of statistical physics except for the fact that the equilibrium state corresponds to a stationary situation. Thus, the only thing we need from statistical physics is the equipartition.

To stress the purely mechanical nature of the result one can consider an example of a one-dimensional harmonic oscillator, a particle with mass m attached to a spring of stiffness k whose other end is fixed at the origin, a mechanical, not statistical example. If the total energy of this oscillator is E, the conditional squared velocity is simply $\langle \dot{x}^2|x\rangle = v^2(x) = (k/m)(2E/k - x^2)$ and the probability density to find the particle at position x is $p(x) = C/|v(x)|$, proportional to the amount of time spent by the particle in the vicinity of the point x, and is given by $p(x) = (2/\pi)(2E/k - x^2)^{-1/2}$. Using the Pope–Ching equation (56) and definition (37) we easily obtain $f = -kx$.

Equation (56) gives an important hint about the fact that the concept of the mean force of section 6 works *only* under the assumption of equipartition of the kinetic energy, and also only in Cartesian coordinates[1].

8. Conclusions

In several popular models of statistical physics (the systems in which the interaction between particles can be reduced to mechanical constraints) the internal energy of an allowed configuration does not depend on coordinates, and all relevant coordinates enter the free energy through the entropic term. The corresponding constraint forces, which can often be measured, are then termed 'entropic forces'. These appear as conditional means of the reaction forces corresponding to the constraints. We analysed several simple situations: the cases of an ideal gas in the vessel with a flat boundary, the case of a gas or solution in a vessel with curvilinear boundaries (in both cases the non-holonomic constraints are put by a confining boundary of the system), and a polymer chain (where the constraints are holonomic and put by forces which hold the monomers together) and discussed the relation of these results with general statements of classical mechanics and of statistical physics (equipartition theorem). We hope that such a discussion will help in deeper understanding of the nature of entropic forces, which otherwise seems to be quite mysterious.

---

[1] Although it is normally not stated explicitly, we always use Cartesian coordinates in teaching statistical mechanics. In curvilinear coordinates, the kinetic terms containing generalized momenta could depend on generalized coordinates, and would not factorize. For such systems, the equipartition of energy does not have to hold for the corresponding kinetic degrees of freedom. This leads to the existence of statistical counterparts of inertial forces, which e.g. enter into the so-called Fixman free energy in polymer physics [8].

Appendix

In their original work [9] Pope and Ching derived a second-order differential equation, of which (56) is a particular solution. In the subsequent paper [10], Emily Ching showed that the equation is essentially a first-order one, so that (56) is the only solution of this equation. Reference [11] discusses the connection of this equation with the level-crossing properties of a random process with continuous trajectories, i.e. of whatever process for which the velocity can be defined at each moment, and connects the result with the fact that the probability of finding a particle in x is proportional to the time it spends in the vicinity of x. In what follows we give an adaptation of [10] to show that the result is purely mechanical and relies only on stationarity (which is always the case under equilibrium conditions), and does not go deep into the probabilistic considerations.

Let us assume that our system exists (i.e. is pertinent to measurements) for some very long time T (which will then tend to infinity), during which the trajectory $x(t)$ can relevantly sample the whole accessible domain of x-values. Let us follow the coordinate x and denote by $\xi(t)$ its values at all times. Let us consider a result of a particular measurement undertaken at some time $0 \leqslant t \leqslant T$. We can put down a probability $P(x|t)$ that this one is equal to x at time t:

$$P(x|t) = \delta(x - \xi(t)). \tag{A.1}$$

In this equation t is a parameter, and $P(x|t)$ is a conditional probability of finding the coordinate equal to x provided its measurement takes place at time t. The time derivative of the conditional probability density $P(x|t)$ is

$$\frac{\partial P}{\partial t} = -\dot{\xi}(t)\frac{\partial P}{\partial x} = -\frac{\partial}{\partial x}(\dot{\xi}(t)P) \tag{A.2}$$

since $\xi(t)$ does not depend on x. Let us now define the unconditional probability density

$$P(x, t) = P(x|t)p_t(t) = \frac{1}{T}\delta(x - \xi(t)) \tag{A.3}$$

being a probability density to find a pair (x, t) in a measurement performed at random. Since this differs from $P(x|t)$ only by a constant multiplier $1/T$, it fulfils the same (A.2).

Let us multiply both parts of the equation for $P(x, t)$ by $\dot{\xi}(t)$,

$$\dot{\xi}(t)\frac{\partial P(x, t)}{\partial t} = -\frac{\partial}{\partial x}(\dot{\xi}^2(t)P(x, t)), \tag{A.4}$$

average it over time,

$$\frac{1}{T}\int_0^T \dot{\xi}(t)\frac{\partial P(x, t)}{\partial t}\,\mathrm{d}t = -\frac{1}{T}\int_0^T \frac{\partial}{\partial x}[\dot{\xi}^2(t)P(x, t)]\,\mathrm{d}t, \tag{A.5}$$

perform the partial integration on the left-hand side,

$$\frac{\dot{\xi}(T)P(x, T) - \dot{\xi}(0)P(x, 0)}{T} - \frac{1}{T}\int_0^T \ddot{\xi}(t)P(x, t)\,\mathrm{d}t = -\frac{1}{T}\int_0^T \frac{\partial}{\partial x}[\dot{\xi}^2(t)P(x, t)]\,\mathrm{d}t, \tag{A.6}$$

and note that the first term vanishes for $T \to \infty$ at a typical point (where $P(x, t)$ does not diverge) for all processes for which the velocity is always well defined.

Now we use the Bayes theorem to put the unconditional probability density $P(x, t)$ into a different form:

$$P(x, t) = P(t|x)p_x(x), \tag{A.7}$$

where $p_x(x)$ is the unconditional density that the outcome of a measurement of the coordinate (a measurement that took place at an arbitrary time) is x. This $p_x(x) = p(x)$ is essentially the stationary probability density of x,

$$p(x) = \int_0^T P(x,t)\, dt = \frac{1}{T} \int_0^T \delta(\xi(t) - x)\, dt = \langle P(x|t) \rangle. \tag{A.8}$$

We now introduce expression (A.7) into (A.6) for $P(x,t)$ and perform the integration over t to get the averages:

$$\frac{1}{T} \int_0^T \ddot{\xi}(t) P(t|x) p_x(x)\, dt = \frac{1}{T} \int_0^T \frac{\partial}{\partial x}[\dot{\xi}^2(t) P(t|x) p_x(x)]\, dt. \tag{A.9}$$

We now interchange the sequence of integration in t and differentiation in x:

$$p_x(x) \frac{1}{T} \int_0^T \ddot{\xi}(t) P(t|x)\, dt = \frac{d}{dx}\left[p_x(x) \frac{1}{T} \int_0^T \dot{\xi}^2(t) P(t|x)\, dt \right]. \tag{A.10}$$

The corresponding conditional time averages

$$\frac{1}{T} \int_0^T \ddot{\xi}(t) P(t|x)\, dt = \langle \ddot{x}(t) | x \rangle \tag{A.11}$$

and

$$\frac{1}{T} \int_0^T \dot{\xi}^2(t) P(t|x)\, dt = \langle \dot{x}(t)^2 | x \rangle \tag{A.12}$$

have to be interpreted as the mean values of acceleration and of squared velocity just in the moments when $\xi(t)$ crosses x, and therefore (A.10) can be put into the form

$$\langle \ddot{x} | x \rangle \, p_x(x) = \frac{d}{dx}[\langle \dot{x}^2 | x \rangle p_x(x)] \tag{A.13}$$

whose solution is exactly (56).

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