

DIPARTIMENTO DI FISICA



SAPIENZA
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Einstein on Boltzmann principle

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Einstein's interpretation of Boltzmann

Annalen der Physik **33**, 1275 (1910)

"Boltzmann principle can be expressed by the equation

$$S = \frac{R}{N} \ln W + \text{const.} \quad (1)$$

where S is the entropy, R the gas constant, N Avogadro's number, W is customarily designated as the "probability" of the state with which the entropy value is associated. W is commonly equated with the number of possible ways (complexions) in which the state considered can conceivably be realized. In order to be able to calculate W one needs a complete theory of the system under consideration..... Considered from a phenomenological point of view equation (1) appears devoid of content."

Unpublished manuscript of a conference given by Einstein on November 2, 1910 at the Zürich Physical Society

Seminaire Poincaré, 1 (2005) 213. French translation by B. Duplantier

“La signification principale de la formule de Boltzmann ne réside cependant pas, à mon avis, en ce qu’on puisse grâce à elle calculer l’entropie en présence d’une représentation moléculaire connue. La manière la plus importante de l’utiliser consiste bien plus en ce qu’à l’inverse, à partir de la fonction entropie déterminée empiriquement, on puisse déterminer la probabilité statistique des états individuels à l’aide de la formule de Boltzmann. On acquiert ainsi une possibilité de jauger de combien devie le comportement du système par rapport au comportement requis par la thermodynamique.”

Exemple. Particule en suspension dans un fluide, et qui est un peu plus lourde que le fluide qu'elle déplace

“Une telle particule devrait, d’après la thermodynamique, couler au fond du récipient et y rester. D’après la formule de Boltzmann cependant, une probabilité W va être associée à chaque hauteur z au dessus du fond..... Soient μ la masse de la particule, μ_0 celle du fluide déplacé par elle. De la formule de Boltzmann s’ensuit

$$W = \text{const} \quad e^{-\frac{N}{RT}(\mu - \mu_0)gz} \quad (2)$$

Cette relation a été testée, et s’est trouvée confirmée, par Perrin.”

La loi du mouvement brownien

“La loi du mouvement brownien peut être déduite très facilement de cette relation à cause de sa densité plus grande la particule tombe d’après la loi de Stokes de $D = \frac{g(\mu - \mu_0)}{6\pi\eta P} \tau$ dans le temps τ , où η représente le coefficient de viscosité du fluide et P le rayon de la particule. Une particule qui, à l’orée du temps τ se trouve à la hauteur z , est à l’issue de ce temps τ à la hauteur $z - D + \Delta = z'$ [Δ déplacement brownien]. Comme la loi de distribution d’une particule ne doit pas dépendre du temps, la valeur moyenne de z^2 doit être égale à celle de z'^2 , donc $\overline{(z - D + \Delta)^2} = \overline{z^2}$, ou encore, pour τ assez petit pour pouvoir négliger D^2 , et $\overline{z\Delta} = \overline{z'\Delta} = \overline{D\Delta} = 0$

$$\overline{\Delta^2} = 2\overline{z}D = \frac{RT}{N} \frac{1}{3\pi\eta P} \tau \quad (3)$$

”

Einstein's theory of deviations in the spatial distribution of fluids from a uniform distribution

Annalen der Physik **33**, 1275 (1910)

Start from the general formula

$$dW = \text{const} \cdot e^{-\frac{N}{R}(S-S_0)} d\lambda_1 \dots d\lambda_n \quad (4)$$

For a closed system the elementary work to produce a deviation is $dA = -T_0 dS$ where T_0 is the equilibrium temperature. Therefore $S - S_0 = \frac{1}{T_0} A$. Let ρ_0 the mean density of a homogeneous substance in a cube of side L . Because of the irregularity of the thermal motion the density ρ at a point will generally differ from ρ_0 . Putting $\rho = \rho_0 + \Delta$ we can develop Δ in fourier series. The statistics underlying its fourier coefficients $\Delta_{k,l,m}$ is obtained from (4). Write $A = \int \rho \phi dv$, where ϕ is the work per unit of mass. A calculation in gaussian approximation gives

$$\frac{L^3}{8\rho^3} \frac{\partial^2 \phi}{\partial (\frac{1}{\rho})^2} \overline{\Delta_{k,l,m}^2} = \frac{RT_0}{N} \quad (5)$$

"It should be noted that the omission of the term with Δ^3 etc. is permissible only if $\frac{\partial^2 \phi}{\partial (\frac{1}{\rho})^2}$ for the ideal thermodynamic equilibrium is not too small or even vanishes. The latter case occurs in the case of fluids or liquid mixtures that are exactly in the critical state. However there is no difficulty, in principle, in completing the theory by taking into consideration the terms of higher order in the coefficients. "

Here is the comment of Ornstein and Zernike, Proc. Acad. Sci. (Amsterdam) **17**, 793 (1914)

"The remark of Einstein that there would be no principal difficulty in extending his deduction to a further approximation, is therefore mistaken. On the contrary, the consideration of higher terms so long as the independence is made use of, will not lead to anything."

Transform a notion which is not directly accessible phenomenologically into a definition or a principle

From the 1905 article *On the electrodynamics of moving bodies*

“It is known that Maxwell’s electrodynamics - as usually understood at this time - when applied to moving bodies, leads to asymmetries which do not appear to be inherent in the phenomena. Take, for example, the reciprocal electrodynamic action of a magnet and a conductor. The observable phenomenon here depends only on the relative motion of the conductor and the magnet, whereas the customary view draws a sharp distinction between the two cases in which either the one or the other is in motion.”

“Examples of this sort, together with the unsuccessful attempts to discover any motion of the earth relatively to the ‘light medium’, suggest that the phenomena of electrodynamics as well as mechanics possess no properties corresponding to the idea of absolute rest. we shall raise this conjecture to the status of a postulate”

Einstein theory of equilibrium fluctuations

In Landau-Lifshitz book on statistical mechanics one finds the following formula for the probability of a fluctuation in a system in contact with an environment

$$P \simeq e^{-\frac{R_{min}}{kT_0}} \quad (6)$$

where

$$R_{min} = \Delta E - T_0 \Delta S + P_0 \Delta V \quad (7)$$

is the *minimal work* necessary to produce the fluctuation with a reversible transformation and ΔE , ΔS , ΔV are the corresponding variations of energy, entropy and volume. T_0 , P_0 are the temperature and pressure of the environment.

Nonequilibrium

Einstein's theory of equilibrium fluctuations is, I believe, the first example in physics of a large deviation estimate. A leading idea in recent research on nonequilibrium has been the extension of this type of estimates to fluctuations in stationary states with the aim of defining analogues of thermodynamic functionals. The notion of *minimal work* to create a fluctuation is meaningful also in stationary states. However we may expect a more complex entanglement of the variables describing the system and those related to the environment so that it is unlikely that quantities like U , S can be defined.

We consider a system connected to several reservoirs (the environment), possibly distributed continuously on the surface of the system, characterized by their chemical potentials. The reservoirs are assumed to be much larger than the system so that their state will be essentially constant in time. When the system is put in contact with the environment, after an initial stage we expect that a description in terms of diffusive processes may apply for a wide class of microscopic dynamics.

Out of equilibrium dynamics plays a major role. In fact what distinguishes non-equilibrium is the presence of currents flowing through the system which have to be considered together with the usual thermodynamic variables. To make any progress we thus have to introduce dynamical equations for the macroscopic variables.

Hydrodynamic equations have been derived from models of microscopic dynamics. Ideally we should start from molecules interacting with realistic forces and evolving with Newtonian dynamics. This is beyond the reach of present day mathematical tools and much simpler models have to be adopted in the reasonable hope that some essential features are adequately captured.

Generalized “Boltzmann Principle”

Bertini, De Sole, Gabrielli, J-L, Landim, 2005

The following formula has been proved for a wide class of particle systems. $J(\rho)$ denotes the hydrodynamic current.

$$\begin{aligned} \mathcal{P}((\rho(t), j(t)), t \in [T_0, T_1]) \\ \asymp \exp \{ -\epsilon^{-d} \mathcal{R}_{[T_0, T_1]}(\rho, j) \}, \end{aligned} \quad (8)$$

where

$$\mathcal{R}_{[T_0, T_1]}(\rho, j) = V(\rho(T_0)) + \mathcal{I}_{[T_0, T_1]}(\rho, j). \quad (9)$$

and

$$\begin{aligned} \mathcal{I}_{[T_0, T_1]}(\rho, j) \\ = \frac{1}{4} \int_{T_0}^{T_1} dt \int_{\Lambda} dx [j - J(t, \rho)] \cdot \chi(\rho)^{-1} [j - J(t, \rho)]. \end{aligned} \quad (10)$$

The interpretation of this formula is quite intuitive. The cost of the fluctuation $(\rho(t), j(t)), t \in [T_0, T_1]$ is given by the work necessary to create the initial condition and is proportional to the total energy dissipated by the extra current $j(t) - J(t, \rho)$.

Summary and conclusion

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HAPPY PRODUCTIVE YEARS !