

Quanta of viscosity

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Abstract

It is shown that the viscosity is quantized in h/m quanta, where h is Planck's constant and m denotes the particle mass.

The chaotical motion of classical statistical ensembles consists of fluctuating times τ during which particles move over a fluctuating distance a , such that these movements are independent of time and of each other; consequently, one may write down the conservation of particle density

$$\begin{aligned} n(x, t + \tau) - n(x, t) &= \frac{1}{2}[n(x + a, t) - n(x, t) + \\ &+ n(x - a, t) - n(x, t)] = \frac{1}{2}[n(x + a, t) + n(x - a, t) - 2n(x, t)] \end{aligned} \quad (1)$$

for motion in both directions; whence

$$\partial n / \partial t = (a^2 / 2\tau) \partial^2 n / \partial x^2 \quad (2)$$

which is the diffusion equation with the diffusion coefficient $D = a^2 / 2\tau$ on the average. Similarly, particles moving with velocity v in time τ are given by $nv\tau$ and by

$$\int_0^a d\xi [n(x + \xi/2) - n(x - \xi/2)] \quad , \quad (3)$$

whence the diffusion equation $nv = D(\partial n / \partial x)$ (Fick's law, or $\partial n / \partial t = D \partial^2 n / \partial x^2$ above) with the diffusion coefficient $D = a^2 / 2\tau$ and a^2 the mean square displacement. Even more, half of $n(x - a/2)$ particles move through x over an average distance a in time τ (the other half move through $x - a$), and, similarly, half of $n(x + a/2)$ move through a in opposite direction; therefore $(1/2)[n(x + a/2) - n(x - a/2)] = (a/2) \partial n / \partial x$ particles (per unit volume) move over a distance a ; it follows that $(a^2 / 2\tau) \partial n / \partial x$ particles move per unit time, which equal vn ; one obtains again the diffusion equation with the diffusion coefficient $D = a^2 / 2\tau$.

Equation (1) is Einstein's kinetic equation.[1] It describes the approach to equilibrium over long times and large distances, by slow processes in comparison with the rapid, short fluctuations. This is the relaxation motion, taking place by diffusive motion. The main content of Einstein's kinetic equation is the introduction of the number of transition processes per unit time, and associating each transition process with destruction and creation of a particle, or quanta. Its generality resides in its various forms. For instance, motion with velocity v along one direction is included in (1) by writing

$$\frac{dn}{dt} = \partial n / \partial t + v \partial n / \partial x = \delta n / \tau \quad , \quad (4)$$

where

$$\delta n/\tau = (a^2/2\tau)(\partial^2 n/\partial x^2) . \tag{5}$$

Boltzmann's kinetic equation is also straightforwardly obtained by introducing the momenta distribution; indeed, in general one obtains

$$\begin{aligned} \frac{dn}{dt} &= \partial n/\partial t + \mathbf{v}\partial n/\partial \mathbf{r} + \mathbf{F}\partial n/\partial \mathbf{p} = \delta n/\tau = \\ &= (a^2/2\tau)\Delta n + (\delta p^2/2\tau)\Delta_{\mathbf{p}} n , \end{aligned} \tag{6}$$

for transport velocity \mathbf{v} and force \mathbf{F} , where δp is the amount of variation of the momentum p along one direction; the isotropy of the chaotical movements is not restrictive. The density n is Boltzmann's distribution function over positions and momenta, and $\delta n/\tau$ is the number of collisions per unit time. The classical entropy

$$S = -\frac{1}{(2\pi\hbar)^s} \int d\mathbf{r}d\mathbf{p} \cdot n \ln(n/e) , \tag{7}$$

where s denotes the number of degrees of freedom, increases in time for non-equilibrium, or is maximal in equilibrium; indeed, leaving aside the transport contributions which vanish on surface, one obtains

$$\begin{aligned} \partial S/\partial t &\sim \int (\partial n/\partial t) \ln n \sim \\ &\sim \int (1/n)[(a^2/2\tau)(\partial n/\partial \mathbf{r})^2 + (\delta p^2/2\tau)(\partial n/\partial \mathbf{p})^2] \geq 0 . \end{aligned} \tag{8}$$

A similar proof holds also for other classical motions.

It is worth noting that the above proof is based on fluctuations, which dissipate motion. Close to local equilibrium the fluctuating distance is given by $a^2 = -(1/9v^{4/3})(\partial^2 s/\partial v^2)^{-1}$, where v denotes here the atomic volume (*i.e.* the reciprocal of particle concentration) and s is the entropy per particle. Similarly, $\delta p^2 = m^2 v^2 = mT$, where m is the particle mass and v is the velocity distributed by Boltzmann (or Maxwell's) distribution. The fluctuating time τ is given by $1/\tau = \delta e/nh$, where δe is the energy fluctuation per particle and nh denotes the uncertainty in the mechanical action consisting of n Planck's quanta h of action. The fluctuating energy is given by $\delta e = T\sqrt{c}$, where c is the heat capacity per particle (at constant volume), so that one obtains for the diffusion coefficient $D = a^2/2\tau = -(1/18v^{4/3})(\partial^2 s/\partial v^2)^{-1}(T\sqrt{c}/nh)$. In the molecular limit of the hydrodynamic description one may represent the diffusion coefficient by $D = T/6\pi v^{1/3}\eta$, according to equilibrium equation $nF = T(\partial n/\partial x)$ and Stokes' law $F = 6\pi\eta r v$ for force F acting upon spherical particles of radius r moving in a fluid with viscosity η . Indeed, the variation

$$-\int dx \cdot nF\delta x - T \int dx \cdot n(\partial \delta x/\partial x) = 0 \tag{9}$$

of the free energy vanishes at equilibrium for a dispersion of particles with density n along the x -axis, where $\delta S = N\delta V/V = n\delta x$ is the entropy variation per unit area of the cross section; one obtains the local equilibrium

$$-nF + T(\partial n/\partial x) = 0 , \tag{10}$$

or

$$-nF + \partial p/\partial x = 0 , \tag{11}$$

i.e. the volume force is compensated by the variation of the osmotic pressure. Making use of the representation given above for the diffusion coefficient D one obtains the viscosity $\eta = -(3/\pi)v(\partial^2 s/\partial v^2)c^{-1/2}nh$, and the viscosity per density $\nu = \eta v/m = -(3/\pi)v^2(\partial^2 s/\partial v^2)c^{-1/2}nh/m$. For a classical ideal gas $(\partial^2 s/\partial v^2) = -1/v^2$ and $c = 3/2$, so that $\nu = (1/\pi)\sqrt{6}(h/m)n$, and h/m may be taken as quanta of viscosity. It is worth noting that interaction is assumed here (even for the ideal gas), at least in the number n of quanta of action. Diffusion coefficients for other classical variables are obtained similarly.

It is worth comparing the fluctuating time with the collision time in a classical gas. The number of particles with velocity v and moving along the z -direction per unit time across the unit area of the cross section is

$$d\nu = \frac{N}{V}(m/2\pi T)^{3/2}e^{-mv^2/2T}v_z d\mathbf{v} ; \quad (12)$$

the reduced mass $m \rightarrow m/2$ must be introduced for the same motion with respect to one particle, and, with σ denoting the cross-section of a collision process, one obtains the number of collisions per unit time

$$\nu = \frac{\pi N}{2V}(m/\pi T)^{3/2} \int e^{-mv^2/4T} \sigma v^3 dv \quad (13)$$

for one particle, or $\nu = (4\sigma/v^3)\sqrt{T/\pi m}$. Therefore, the collision time is $\tau_{coll} = 1/\nu \sim (d^2/\sigma)d\sqrt{m/T}$, where the mean inter-particle separation $d = v^{1/3}$ has been introduced. The mean free path is given by $l = v\tau_{coll} \sim (d^2/\sigma)d$. The gas is classical providing $n\lambda^3 \ll 1$, where $\lambda \sim h/\sqrt{mT}$ is the thermal wavelength, or $d\sqrt{mT} \gg h$, *i.e.* the classical action be much larger than quanta of action. It follows that $\tau_{coll} \sim (d^2/\sigma)(1/T)d\sqrt{mT} \sim (d^2/\sigma)\tau(d\sqrt{mT}/nh)$, where τ is the fluctuating time. The classical action $d\sqrt{mT}$ is however much larger than the fluctuating action nh , so that $\tau_{coll} \gg \tau$ ($d^2/\sigma \gg 1$ also), *i.e.* the collision time is much longer than the fluctuating time, as expected. This is to be completed with $\tau \gg h/T$, *i.e.* the statistical fluctuating time is much longer than the quantal fluctuating time. Similarly, the quantal elementary excitations have a much longer lifetime than τ , and τ_{coll} above may be viewed as the lifetime of a classical particle.

The evolution of the quantal distribution of probability ρ_n (diagonal elements of the density matrix) is given by the master equation

$$\partial\rho_n/\partial t = \sum_m (T_{nm}\rho_m - T_{mn}\rho_n) , \quad (14)$$

where T_{nm} is the transition probability per unit time from state n to state m ; Einstein's kinetic equation is easily recognizable here. Close to equilibrium T_{nm} are given by the second-order perturbation theory as

$$T_{nm} = \frac{2\pi}{\hbar} |V_{nm}|^2 \delta(E_n - E_m - \hbar\omega) , \quad (15)$$

where V_{nm} are the matrix elements of the perturbation V , $E_{n,m}$ are the corresponding energies, and $\hbar\omega$ is the transferred elementary quanta. The transition probability T_{nm} is symmetric and positive. The entropy $S = -\sum \rho_n \ln \rho_n$ evolves in time according to

$$\partial S/\partial t = (1/2) \sum T_{nm}(\rho_m - \rho_n)(\ln \rho_m - \ln \rho_n) \geq 0 , \quad (16)$$

i.e. it increases with time. In the quasi-classical description the states m in (14) are close to n , and the transition probability may be written as $T_{nm} \sim |V|^2/\hbar\delta E$; the minimal uncertainty reads $|V|\tau = h/2$, where τ is the fluctuating time, so that the transition probability becomes $T_{nm} = \pi/2n_c\tau$, where n_c from $\delta E\tau = n_c h$ is the range of m -states in the neighbourhood of n ;

in addition, the distribution of probability can be expanded as $\rho_m = \rho_n + (m - n)(\partial\rho_n/\partial n) + (1/2)(m - n)^2(\partial^2\rho_n/\partial n^2) + \dots$, so that (14) becomes

$$\partial\rho/\partial t = \frac{\pi}{2n_c\tau} \int dn \cdot (1/2)n^2(\partial^2\rho/\partial n^2) \simeq (n_c^2/2\tau)(\partial^2\rho/\partial n^2) . \quad (17)$$

For states n corresponding to position for instance, one recovers the classical equation of diffusion $\partial n/\partial t = (a^2/2\tau)(\partial^2 n/\partial x^2)$. Indeed, the distribution ρ is proportional to the particle density in the classical limit (the matrix elements nm are the $(n - m)$ -Fourier transforms, and the states are described by position, momentum, and the rest of classical variables). It is worth noting here that approaching equilibrium by fluctuations is meaningful for statistical ensembles only, as expected, *i.e.* for ensembles with a large number of degrees of freedom (including wavevectors, as for fields), where the quasiclassical description works.

It is also worth noting that the usual kinetics, *i.e.* transport, either classical or quantal, proceeds over long times and large distances, being limited, first, by carriers' lifetime (and the corresponding mean free path), and, secondly, by fluctuations, both statistical and quantal, in principle. In such a context, it is described by the continuity equation, which is the starting point of Einstein's kinetic equation too, where, however, a represents the mean free path and τ represents the lifetime, or collision time.

The chaotical character of the statistical motion implies the "detailed balancing principle", by which the number of direct transitions ("Wiedereinwands") equals the number of reverse transitions ("Umkehreinwands"), Boltzmann's "H-theorem" of increase of the entropy ("H-function"), as well as the object of the "ergodic (or quasi-ergodic) theorem", by which the relevant states have a non-vanishing probabilistic measure; and contains the irreversibility in addition and superimposed over the reversible mechanical motion ("Loschmidt's objection"); their compatibility being ensured through interaction, and external, like initial and boundary, conditions.

References

- [1] A. Einstein, Ann. Physik **17** 549 (1905); **19** 371 (1906); Z. Elektrochemie **14** 235 (1908).