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# THE QUANTUM THEORY OF THE EQUATION OF STATE

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## Abstract

It is shown that the quantum theory analogue to the quantity $e^{-\epsilon_{pot}/kT}$ giving the distribution in coordinates of systems at temperature $T$ can be easily set up. Similarly in quantum theory the computation of the free energy can be reduced to the integration of such a function over the coordinates, as in classical theory. The result is applied to a qualitative discussion of the equation of state of an imperfect gas, showing that He and $H_2$ may be expected to show quantum effects in their equations of state, but hardly any other gases.

QUANTUM statistics have been mostly developed on the basis of the older quantum theory, rather than of wave mechanics. As a result of this, full use has not been made of the essentially statistical form of the present quantum mechanics. It is the purpose of the present note to point out how naturally, and simply, in principle at least, one can treat such problems as the equation of state of an imperfect gas by quantum theory. As a preliminary, we discuss the analogue in quantum theory to the expression $e^{-\epsilon_{pot}/kT}$ in classical statistics, giving the probability of finding a system, at temperature $T$, in a position where the potential energy is $\epsilon_{pot}$.

Suppose we have given a wave function $\psi$. Then by the fundamentals of the statistical interpretation of quantum mechanics, the probability of finding a system of the sort described by $\psi$, in the small element of volume $dq_1 - dq_n$, is $\psi^*\psi dq_1 - dq_n$. If, in particular, $\psi = \Sigma_i C_i u_i(q_1 - q_n)e^{-(2\pi i/h)E_i t}$, then the probability becomes $\Sigma_{ij} C_i^* C_j u_i^* u_j \, e^{-(2\pi i/h)(E_i - E_j)t} \, dq_1 - d8_n$. By either of two procedures, we can eliminate the terms varying with time $(i \neq j)$: we can average over time; or we can assume that we have sort of an ensemble of $\psi$'s (each separate $\psi$ being almost as general as a whole ensemble in classical statistics), in which the different $C_i$'s are statistically independent in phase, and we can average over this ensemble. In either case, the result is that the remaining terms of the probability are $\Sigma_i C_i^* C_i u_i^* u_i dq_1 - dq_n$, or, if the $c$'s and $u$'s are real, $\Sigma_i C_i^2 u_i^2 (q_1 - dq_n) dq_1 - dq_n$.

On the other hand, given a classical distribution function $f(q_1 - q_n, p_1 - p_n)$ giving the probability of finding the system in a given point of phase space, we can at once pass to the probability of finding it at a given point of coordinate space by integrating over momenta: $[\int - \int f \, dp_1 - dp_n] \, dq_1 - dq_n$. This should then correspond to the quantum expression of the last paragraph.

In particular, in thermal equilibrium at temperature $T$, we assume in either classical or quantum statistics the canonical ensemble. In classical statistics, this is given by $f = \text{constant} \times e^{-\epsilon(q_1 - p_n)/kT}$, where $\epsilon(q_1 - p_n)$ is the energy as function of coordinates and momenta. If, as in ordinary mechanical problems, $\epsilon=\epsilon_{pot}\ (q_1-q_n)+\Sigma p^2/2m$, then we can carry out explicitly the integration over the momenta, and the result is that the probability of finding the system in $dq_1-dq_n$ is constant $\times\Pi_n(2\pi mkT)^{1/2}\times e^{-\epsilon_{pot}/kT}\ dq_1-dq_n$, the product being over all degrees of freedom. Thus, at constant temperature, the distribution in space is given by $e^{-\epsilon_{pot}/kT}$.

In quantum mechanics, on the other hand, the canonical ensemble is given by supposing that the number of systems in the $i^{th}$ stationary state is proportional to $e^{-E_i/kT}$, (all degenerate levels being separately counted). It is to be noted that this is true, quite apart from the question as to whether the system obeys Boltzmann, Einstein-Bose, or Fermi-Dirac, statistics. The latter arise from the existence of identical particles within the system, they show themselves only in changing the allowed stationary states, and appear as a change in the statistics only when viewed in the $\mu$ space, not as we are working here in the $\Gamma$ space. Now the number of systems in the $i^{th}$ state is proportional to $C_i^2$. Hence on quantum mechanics the probability of finding a system at $q_1-q_n$ is $\Sigma_i e^{-E_i/kT}u_i^2(q_1-q_n)\ dq_1-dq_n$. It is this function which should agree with the classical expression above. As a matter of fact, we can get complete agreement if we divide the classical expression by $h^n$. Thus we should have

$$\prod_n\left(\frac{(2\pi mkT)^{1/2}}{h}\right)e^{-\epsilon_{pot}/kT} = \sum_i e^{-E_i/kT}u_i^2(q_1\cdots q_n).$$

The relation above may be expected to hold only in the limiting case of high quantum numbers; for it is a form of correspondence between classical and quantum distributions. Thus we expect that, for low temperatures, where only low states are excited, it will be a very inperfect correspondence; but at high temperatures it should become more and more exact. We may show the actual nature of the agreement by examples.

Suppose we consider a collection of systems, each consisting of a single particle of mass $m$ moving in a one dimensional box of length $L$, the potential being zero while the particle is in the box, infinite outside. Then the normalized wave functions are $u_n(x)=(2/L)^{1/2}\sin n\pi x/L$, and the energies are $E_n=n^2h^2/8mL^2$. Our distribution function on classical theory is then $(2\pi mkT)^{1/2}/h$ within the box, zero outside. On quantum theory it is

$$\sum_{n=1}^{\infty} e^{-n^2h^2/8mL^2kT}\ \frac{2}{L}\sin^2\frac{n\pi x}{L}$$

within the box, zero outside. In Fig. 1, we plot this function for various temperatures, comparing with the constant classical value. It is seen that in the center of the box, for reasonably high temperatures, the quantum distribution approaches the classical one extraordinarily closely. Near the boundary, however, this is not true. The reason is that in the center there are waves superposed in all sorts of phases, and only their amplitudes are of significance, not their wave-lengths. Near the edges, however, on account of the fact that all waves reduce to zero on the boundary and are hence in phase, there is a sort of interference, and within a wave-length of the edges the distribution shows characteristic quantum effects. If the temperature is $T$, and the average kinetic energy $\frac{1}{2}kT$, then a sort of average wave-length is given by setting $p^2/2m=\frac{1}{2}kT$, $\lambda=h/p=h/(mkT)^{1/2}$. Thus the distance in which the distribution is anomalous is independent of the size of the box, and depends only on the mass of the particle and the temperature. For example, for a hydrogen atom at 100°K, the distance is 3.69A. The exact distribution around an edge of the box can be found, in the limiting case when $L$ is large. For then, for small $x$ compared with $L$, the summation can be replaced by an integration:

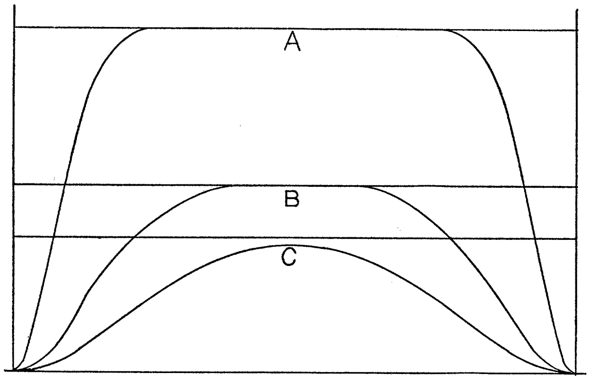

Fig. 1. Curves $\int e^{-\epsilon/kT}dp=f(T)e^{-\epsilon_{pot}/kT}$ for a free particle in a box (straight lines) and the quantum analogy to the same quantity (curves) as functions of position in the box. Temperatures are so chosen that in ($A$) there are 0.9 as many particles in the second quantized state as in the lowest state, in ($B$) 0.7, and in ($C$) 0.5 as many.

$$\int_0^\infty e^{-n^2h^2/8mL^2kT}\frac{2}{L}\sin^2\frac{n\pi x}{L}\,dn=\frac{(2\pi mkT)^{1/2}}{h}\left\{1-\exp\left[-8\pi^2\left(x\frac{(mkT)^{1/2}}{h}\right)^2\right]\right\}.$$

For $x$ large compared to $h/(mkT)^{1/2}$, the exponential reduces to zero, and we have the classical, constant value. On the other hand, for $x$ small, the distribution decreases to zero at the boundary.

Similarly in Fig. 2 we plot several distribution curves, obtained from the two methods, for the linear oscillator. Here there is not such marked possibility of interference as with a sharp wall of potential, and the two methods agree more exactly. It is only at quite low temperatures, when only the lowest state is appreciably excited, that there is large discrepancy. Here the quantum distribution is of course simply that of the lowest vibrational level.

These two examples should indicate that in general, the quantum distribution agrees with the classical one except at such low temperatures, and correspondingly long average wave-length, that the potential changes greatly in a single wave-length. We can in fact give a simple proof of this by the method of Kramers, Wentzel, etc., worked out for this case by Van Vleck.[1]

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[1] Van Vleck, Proc. Nat. Acad. Sci., **14**, 178 (1928).

This method treats the amplitude of the wave function, showing how it varies with the potential. VanVleck shows, for a general mechanical system, that $u_i^2(q_1 - q_n)$, if we take the average over the sinusoidal oscillations of the function, is proportional to the limit to the integral over the momenta of the distribution $f(q_1 - q_n\ p_1 - p_n)$ for a microcanonical ensemble of energy $E_i$. Since our summation $\Sigma_i e^{-E_i/kT} u_i^2$ corresponds to a canonical ensemble made up of microcanonical ones of all different energies, it would then be proportional to the integral over momenta of the distribution $f$ for a canonical ensemble, which is what we wished to show.

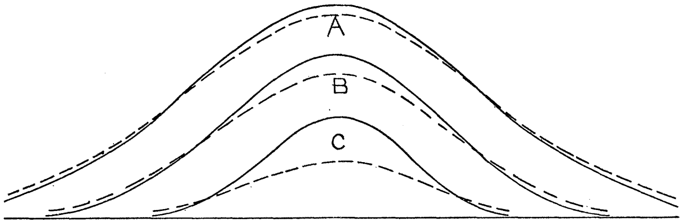

Fig. 2. Curves $f(T)e^{-\epsilon_{pot}/kT}$ for a linear oscillator (full lines) and quantum analogy to the same quantity (dotted lines) as function of displacement from position of equilibrium. Temperatures are chosen so that in $(A)$ there are 0.5 as many oscillators in each state as in the one below, in $(B)$ 0.3, in $(C)$ 0.05 as many.

Having discussed the analogue of the Boltzmann function $e^{-\epsilon_{pot}/kT}$ in quantum theory, we can proceed to the related problem of the equation of state. This is ordinarily found by computing the free energy $\psi$, given by the equation

$$e^{-\psi/kT} = \frac{1}{h^n}\int - \int e^{-\epsilon/kT} dq_1 \cdots dp_n$$

or

$$= \sum_i e^{-E_i/kT}$$

on classical and quantum theory, respectively. Then by differentiating $\psi$, we can find specific heat and pressure. The quantum form has been often used for computing specific heat, but not for equation of state. For the latter purpose, with the classical form, we ordinarily integrate first over the momenta, obtaining

$$\prod_n \frac{(2\pi m k T)^{1/2}}{h} \int - \int e^{-\epsilon_{pot}/kT} dq_1 \cdots dq_n.$$

The integral over the coordinates is then evaluated. For an imperfect gas at low density, for example, $\epsilon_{pot}$ is zero in most parts of the coordinate space, and $e^{-\epsilon_{pot}/kT} = 1$. Only in those particular regions of space where two atoms are close together do we have an integrand different from unity. By considering only single collisions, as in the computation of the second virial coefficient, we can consider separately the various parts of coordinate space where two molecules are in collision, reducing the whole problem to a set of separate ones each dealing with a single collision, and these can be easily treated. The problem leads eventually to the valuation of an integral $\beta = \int\int\int(1 - e^{-\epsilon_{pot}'/kT})\,dv$, where $\epsilon_{pot}'$ is the potential energy of one molecule in the field of another fixed one. In terms of $B = (N/2)\beta$, when $N$ is the number of molecules, the final result is

$$e^{-\psi/kT} = \left(\frac{(2\pi mkT)^{1/2}}{h}\right)^{3N}(V - B)^N,$$

$\psi = -(3N/2)kT \log (2\pi mkT/h^2) - NkT \log (V - B)$, from which

$$C_v = -T\left(\frac{\partial^2\psi}{\partial T^2}\right)_V = (3/2)Nk, \quad P = -\left(\frac{\partial\psi}{\partial V}\right)_T = \frac{NkT}{V - B}\,.$$

In the quantum theory, in a corresponding way, we may write $e^{-\psi/kT}$ as an integral over coordinates. We do this by substitution of $\Sigma_i e^{-E_i/kT}u_i^2(q_1 - q_n)$ for the corresponding classical expression $\Pi_n(2\pi mkT)^{1/2}/he^{-\epsilon_{pot}/kT}$. The result is then

$$e^{-\psi/kT} = \int \sum_i e^{-E_i/kT}u_i^2(q_1 \cdots q_n)dq_1 \cdots dq_n$$

by exact analogy with the classical case. Taking the summation outside, integrating, and making use of the normalization of the $u$'s, this reduces at once to the form $\Sigma_i e^{-E_i/kT}$ given above. But in practice it is more practicable not to do this, but to proceed as in the classical case. For the imperfect gas, for example, we know at once that the quantum density distribution approaches the classical except where the potential changes greatly in a single wave-length. Thus our integrand is practically $\Pi_n(2\pi mkT)^{1/2}/h$, throughout the whole of configuration space except on the walls of the vessel (which is unimportant) and in the regions where two molecules are in collision. The whole argument of separating out the different colliding pairs goes through as in classical statistics, and the only change comes when we compute $\beta$. Then, instead of putting in the classical expression $e^{-\epsilon_{pot}'/kT}$ for the interaction of a pair of molecules, we must use the corresponding quantum theory value. To work this out, we must solve the problem of the interaction of two molecules. If for example they are monatomic, or for any other reason spherically symmetrical, this problem will be one of two particles acting on each other by central forces, which can be solved, if necessary by numerical methods, when the interatomic potential is known. Having found the stationary states and wave-functions (including of course the continuous ones), we square, multiply by the corresponding $e^{-E_i/kT}$ and add. The resulting distribution will be similar to $e^{-\epsilon_{pot}'/kT}$, and must be used in its place.

The actual calculation, as we readily see, is much more tedious than in classical mechanics, since it involves finding many wave-functions. It is then fortunate that in general the results will agree closely with those of classical mechanics, so that a classical calculation suffices. We can see this by examining the potential curve for the interaction of the molecules. The potential will of course have a negative region, where the molecules attract, and then at shorter distances they all repel. There will be in general discrete vibrational and rotational states, of negative energy, and continuous ones of positive energy. We can get a very rough idea of the number of vibrational levels as follows: it should equal $\int pdq/h$, where the integral is over the region where the potential is definitely negative. If we let the length of this region be $L$, and let $\bar{p}$ be a sort of average $p$, the result is $2L\bar{p}/h$. But now take the worst case, where the particles on separation have no kinetic energy. Then $p$ is related to the energy of dissociation of the aggregate of two molecules, and this energy is approximately given by the critical temperature, so that very roughly we may write $\bar{p}=(mkT_c)^{1/2}$. Thus this approximation gives $[2L(mkT_c)^{1/2}/h]$ for the number of levels. If we take $L=3$A, a reasonable value, and substitute numerical values, we have $0.162\ (MT_c)^{1/2}$, where $M$ is the molecular weight. Thus for He we have less than one state, for $H_2$ one only, for Ne 4 or 5, for $N_2$ 9 or 10. The result for He can be checked from the actual potential, and calculation actually seems to show that no discrete levels exist. The other values are highly tentative, but probably of the right order of magnitude. Thus we see that, with the exception of He and $H_2$, the other gases all have several vibrational levels, which of course are all excited under ordinary conditions in the gas above the critical point. We may anticipate then that for all gases except these two, the wave-length is short enough in proportion to the size of the potential minimum, and the states are sufficiently excited, so that classical statistics will give a good approximation.

For the two light gases, however, and particularly for He, we shall expect deviations from the classical statistics of molecular interaction. This has already been noticed by London,[2] without however indicating the proper method of correcting it. It is evident, as London points out, that on account of the lack of negative levels, the attraction cannot be as effective as it would be classically, and the second virial coefficient $B$ must be larger than if we used a classical calculation. It is no doubt significant in this connection that the values of $B$ for He, as computed by Kirkwood and Keyes,[3] using classical statistics, lies below the experimental values, at low temperatures. It is to be hoped that a detailed calculation, using quantum statistics, will show an improvement of the agreement.

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[2] F. London, Zeits. f. Physik **63**, 259 (1930).

[3] J. G. Kirkwood and F. G. Keyes, Phys. Rev. 37, 832 (1931).