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Note on Statistical Forces

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It is shown that a two-particle force acting in coordinate space represents with a very good approximation the apparent coupling in space between two spinless atoms of ideal symmetrical or antisymmetrical assemblies at all temperatures higher than, or equal to, their transition temperature.

THE equation of state of ideal Bose-Einstein (B.E.) or Fermi-Dirac (F.D.) gases above and at their transition temperature, described by the sum of an infinite series of virial coefficients, corresponds to one of the several aspects of the statistical forces acting between the spinless point atoms forming these gases. In non-ideal classical gases, in whose Hamilton function the kinetic energy is the sum of the individual kinetic energies of the atoms, and the potential energy is the sum of two-particle or two-atom interaction energies, the equation of state is described also¹ by an infinite series of virial coefficients. Assume then for a moment that the virial coefficients of the ideal quantum gases are, from the third one on, all very small in comparison to the first and second virial coefficients. If, moreover, the ratio

$$\rho(T) = \left| \sum_{k \geq 3}^{\infty} \Phi_k(T) \right| / |\Phi_2(T)|,$$

where Φ_k denotes the k th virial coefficient at temperature T , were also a small number, then it would appear justified to search for such a two-atom interaction energy which, when introduced into the Hamilton function of a classical ideal gas, would lead to the exact first and second virial coefficients of the ideal quantum gases without leading to exact values of the small negligible virial coefficients of order higher than the second. Such a two-particle interaction taking place in coordinate space could then be regarded as representing, with a very good approximation, the actual forces existing in space between the atoms of these gases by virtue of their respective symmetry in phase space.

¹ Cf. J. E. Mayer, *J. Chem. Phys.* **5**, 67 (1937).

These forces have already been derived² incidentally by simply identifying the approximate relative probability densities in configuration space of the quantum gases of spinless atoms with that of a classical non-ideal gas having the type of Hamilton function just mentioned, namely, with the total potential energy represented by the sum of two-particle interaction energies depending on the distance of the coupled atoms. It seemed interesting, however, to rediscuss shortly these forces, in particular, in the B.E. case, around the transition temperature of the quantum gases. We should like to show that these statistical forces represent with a good approximation the apparent interaction, in coordinate space, of the atoms of these ideal quantum gases at all temperatures $T \geq T_0$, T_0 being the transition temperature of the gases. A rough but reasonable estimate of these forces can also be given for temperatures $T < T_0$.

Indeed, the conditions indicated above concerning the virial coefficients of the gases, and which justify these statistical forces, are fulfilled for both B.E. and F.D. ideal assemblies of spinless atoms at all temperatures $T \geq T_0$.

Consider first the B.E. gas. Since the ratio $\rho(T)$ is a smoothly decreasing function of T , it has to be evaluated at T_0 , the transition temperature, where it has the largest value. One finds thus,³

$$\rho_{\text{B.E.}}(T_0) = 0.0537,$$

which is quite small and indicates that it should be possible to represent with a good approximation the forces of statistical origin acting in coordinate space with a two-particle force.

² Cf. G. E. Uhlenbeck and L. Gropper, *Phys. Rev.* **41**, 79 (1932).

³ The first four virial coefficients have been given by Einstein, *Ber. d. Berl. Akad.* **3** (1925).

In the case of ideal F.D. gases⁴ one finds that

$$\rho_{F.D.}(T_0) = 0.0141,$$

the smallness of which, as compared to $\rho_{B.E.}(T_0)$, is due in part to the alternating signs of the virial coefficients beginning with Φ_2 which is positive. One finds moreover that even the ratio

$$\bar{\rho}_{F.D.}(T_0) = \sum_{k \geq 3}^{\infty} |\Phi_k(T_0)| / |\Phi_2(T_0)|$$

is a small number and a generous estimate of its upper limit appears to be less than 0.030. Here, too, therefore, the approximate two-particle statistical force is entirely justified. This force is only approximate since it does not lead to the exact virial coefficients of all order, giving only the first two correctly. This shows that a two-particle force in coordinate space cannot describe correctly the statistical interaction resulting from the imposed symmetry in phase space of these systems.

The physical meaning of the smallness of the ratios $\rho_{B.E.}$ and $\bar{\rho}_{F.D.}$ corresponds to the fact that the atoms of these ideal quantum gases have practically no tendency to form anything but very small clusters, clusters of single atoms and of pairs of atoms.

The forces in question are²

$$V_{B.E.}(r, T) = -kT \log (1 \pm \exp - [2\pi(r/\lambda)^2]),$$

F.D.

where k is Boltzmann's constant, r is the separation of two atoms, λ is the de Broglie wave-length associated with their average thermal motion, $\lambda = h/(2\pi mkT)^{1/2}$ the positive and negative signs in the argument of the logarithm correspond, respectively, to the symmetrical and antisymmetrical interaction. $V_{B.E.}(r)_T$ at constant T is a bell shaped potential energy well; $V_{F.D.}(r)_T$ resembles the usual repulsive interactions. The discussion of these interactions at constant T as well as the interactions $V_{B.E.}(T)_r$ and $V_{F.D.}(T)_r$, with the separation r kept constant, leads without difficulty to the determination of the limitations of the validity of these forces. This discussion will be omitted here. These forces cannot be applied directly at temperatures $T < T_0$ because

the method used in their derivation is valid only above T_0 . A reasonable estimate below T_0 appears to correspond to a temperature independent force, with T_0 substituted for T and λ_0 for λ in the above expression of these forces. The origin of this estimate lies in the fact that the $V(T)_r$ interactions show a tendency to decrease and vanish with temperature below some temperature $T_m(r)$ depending on r . This trend of the statistical forces has no physical meaning and one is led thus to adopt, below T_0 , their expression corresponding to T_0 , at least at all those larger distances for which $T_m \leq T_0$. At those smaller distances for which $T_m > T_0$, it is this temperature T_m which plays the role of T_0 .

Having justified the applicability of the ideal statistical two-particle forces, it seems interesting to compare them directly to forces of another nature acting between particles forming a given system. We should like to compare the inter-atomic force between two helium atoms⁵ with the symmetrical statistical two-particle force around the transition temperature in the liquid under its saturated vapor pressure at 2.19°K. It is clear that the force $V_{B.E.}(r, T)$ is rather a lower limit since it has been obtained with the free particle wave functions. It can be shown now that this free particle statistical force is valid for distances extending from well below the position of the minimum in the inter-atomic force—around 3Å—to larger distances. One finds thus that the ideal statistical force is roughly twenty times smaller than the inter-atomic force in quite a large interval of separation around the above indicated position of minimum. One might say here that if B.E. statistics were playing an important role in the peculiar transition effect at 2.19°K, then the more exact liquid wave functions could eventually lead to a two-particle non-ideal statistical force whose order of magnitude would be nearer to that of the inter-atomic force. No definite conclusion can naturally be based upon the preceding comparison between the two forces as to their relative importance. Nevertheless, the above ratio of twenty appears quite large. It should be remembered, on the other hand, that no matter how small the statistical

⁴ The numerical values of F. D. functions given by J. McDougall and E. C. Stoner, Phil. Trans. **237**, 64 (1938) were used here.

⁵ Cf. J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).

force is compared to the inter-atomic force it assures an Einstein transition. The preceding comparison seems to indicate that a treatment of the non-ideal helium gas on the basis of the ideal B.E. fluid, where the non-ideal character, i.e., the inter-atomic force, is considered as a perturbation, cannot well be justified. The treatment where the non-ideal classical fluid is taken as the zero-order approximation, and where the

symmetry in phase space would be considered as a perturbation, might lead to more plausible results.

Similar results have been obtained recently⁶ through detailed and laborious studies on the theory of the second virial coefficient of helium at low temperatures.

⁶ Cf. J. De Boer and A. Michels, *Physica* **9**, 409 (1938) and also B. Kahn, Dissertation, Utrecht (1938).

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The Photolysis of Persulfate*

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The photochemical efficiency, ϕ , for the decomposition of persulfate by light of $\lambda 254\text{ m}\mu$ is determined by comparison with ϕ for the uranyl oxalate actinometer. The persulfate content was followed by the method of Kurtenacker and Kubina and in representative cases the hydrogen ion produced also was determined. The equation $\text{S}_2\text{O}_8^{2-} + \text{H}_2\text{O} + h\nu = 2\text{HSO}_4^- + \text{O}_2/2$ accounts quantitatively for the data. Evidence is given to show that the main reaction is not the decomposition of SO_4^- . Six tenths of a mole of persulfate is decomposed per Einstein absorbed by persulfate in dilute neutral and alkaline solutions when all oxidizable material is absent. Acetic acid increases this yield to unity but non-oxidizable ions have a depressing effect. Many of the observations of Morgan and Crist also are verified. At constant ionic strength, ϕ remains nearly unchanged in alkali, but drops abruptly to less than 0.01 when solutions are acidified suggesting the formation of a weak acid containing photochemically inert persulfate. Absorption spectra and conductivity measurements, however, give no indication that such a weak acid is formed. The explanation offered for these facts is that the hydrogen ion associates with and thereby stabilizes the persulfate ion after the latter absorbs a photon. The stabilizing effects of other ions, except perhaps bisulfate, is much less than hydrogen which is thought to be related, among other things, to their larger size. Hydrogen peroxide was not found in any of the solutions.

ULTRAVIOLET light of $\lambda 254\text{ m}\mu$ decomposes colorless aqueous solutions of persulfate, the reaction $\text{H}_2\text{O} + \text{S}_2\text{O}_8^{2-} + h\nu = 2\text{HSO}_4^- + \text{O}_2/2$ accounting quantitatively for the increase in acidity accompanying the loss of persulfate¹ as found in experiments 9c and 12 summarized in Table I and in the text under H^+ ion yields.

Crist² precipitated the liberated sulfate as the barium salt and found it corresponded to the loss of one mole of persulfate per Einstein absorbed

at $\lambda 302$, 265, and $254\text{ m}\mu$ by $0.05M\text{ K}_2\text{S}_2\text{O}_8$ when the solution undergoing photolysis was alkaline or had not been acidified. The presence of electrolytes decreased¹⁻⁴ the photochemical efficiency, ϕ , sulfuric acid being especially effective.

Since this work, Kurtenacker and Kubina⁵ have improved greatly the method for determining persulfate. Their method as used in this research gives values for ϕ about 0.6 as large as

* Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 493.

¹ J. L. R. Morgan and R. H. Crist, *J. Am. Chem. Soc.* **49**, 960 (1927) mentioned this fact but gave no data.

² R. H. Crist, *J. Am. Chem. Soc.* **54**, 3939 (1932).

³ J. L. R. Morgan and R. H. Crist, *J. Am. Chem. Soc.* **49**, 16 (1927).

⁴ J. L. R. Morgan and R. H. Crist, *J. Am. Chem. Soc.* **49**, 338 (1927).

⁵ A. Kurtenacker and H. Kubina, *Zeits. f. anal. Chemie* **83**, 14 (1930).