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# Transport Phenomena in a Bose-Einstein Gas

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This paper develops the formal first order perturbation theory of transport phenomena in an ideal Bose-Einstein gas.

The perturbation relaxation time is an unknown parameter in the theory. The ratio of thermal conductivity to viscosity is independent of this relaxation time; it increases discontinuously by a factor almost 2 at the Bose-Einstein condensation temperature $T_\lambda$. The isothermal Knudsen heat of transport through a small hole, classically equal to $2kT$, drops rapidly to zero as $T$ falls to $T_\lambda$: the Bose-Einstein gas flowing isothermally through a small hole carries no heat when its temperature is below $T_\lambda$ and it exhibits corresponding thermo-mechanical effects.

The mathematical analysis is carried out in terms of an approximation in which the lowest energy states of the gas are treated discretely while above an arbitrary level they are treated by an integration approximation. The treatment is capable of generalization to models in which there are anomalies in the lowest level spacings.

## INTRODUCTION

As briefly reported previously[1] the transport phenomena in an ideal Bose-Einstein gas show some interesting analogies with the peculiar phenomena in liquid helium II. In the previous work only the first approximation was used, namely the integration approximation familiar in discussions of the equilibrium properties of the Bose-Einstein gas.[2] Here we proceed to the second approximation and include a finite (arbitrary) number of the lowest states from zero up to $\epsilon_z$ summed discretely. The transition temperature $T_\lambda$ at which condensation in momentum space sets in depends on the energy $\epsilon_z$ chosen, and this dependence is examined in some detail.

Velocity distribution functions are set up and first order perturbations are defined. Boltzmann equations for the rate at which these perturbations tend to be removed by collisions are expressed in terms of a relaxation time $\tau_n$. This relaxation time could in principle be calculated from quantum theoretical considerations if a definite model were adopted for the atomic forces.[3] However such a calculation would involve considerable speculation especially with regard to the collision cross section of the particles condensed into the lowest state.[4] We therefore confine ourselves to a formal development in terms of $\tau_n$ as an unknown parameter.

The perturbations here considered are such that the total number of particles in any given energy range of the continuous spectrum or in any one level in the discrete spectrum remains constant and equal to the equilibrium number. It is the spherical symmetry of the velocity distribution in each such range or level that is perturbed. It is implied here, as in all classical first-order perturbation theory, that the relaxation time of such perturbations is long compared with the relaxation time for adjustment of equilibrium between the numerical populations of the various states. This assumption may in fact be invalid below the transition temperature where, according to ideas expressed elsewhere,[5] the transition probabilities between the lowest state and the excited states may become so low that even perturbations like time dependent variations of temperature may necessarily involve disturbances of equilibrium in the numerical distribution. We shall not consider this kind of complication in the present discussion.

The energy per particle in the lowest energy state may be assumed independent of the population in that state. This is consistent with the picture of an ideal gas in an infinite enclosure and essential to the validity of statistical formulas. Under this assumption the first-order perturbation theory leads formally to the interesting result that below the transition temperature a temperature gradient produces a mass flow which cannot be prevented by any opposing pressure gradient. This is because below the temperature $T_\lambda$ the condensed particles exert no pressure and the pressure of the excited particles is a single valued function of temperature and independent of the density of the gas. The temperature gradient causes excited particles to flow along with the heat current and condense into the lowest state at the point of heat removal; but there is no mechanism provided for the return flow of the lowest-state particles in spite of the concentration gradient set up. However admitting that the particles have finite size and that the energy of the lowest state is not entirely independent of its population, we are able to imagine

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[1] W. Band, Phys. Rev. **75**, 339A (1949).

[2] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940).

[3] E. A. Uehling and G. E. Uhlenbeck, Phys. Rev. **43**, 552 (1933); E. A. Uehling, Phys. Rev. **46**, 917 (1943).

[4] J. de Boer and J. van Kranendonk, Physica **XIV**, 442 (1948); J. de Boer, Physica **X**, 348 (1943).

[5] L. Meyer and W. Band, Phys. Rev. **74**, 386, 394 (1948).

that the concentration gradient of lowest-state particles will drive them up the temperature gradient and so balance the mass flow of the excited particles down the temperature gradient.

The thermal conductivity of such a model is found to increase by a factor of about 2 as $T$ drops through $T_\lambda$, but then to drop rapidly with further decrease of temperature. There is no superconductivity for heat in the ideal Bose-Einstein gas.

The viscosity of the gas is found to equal the product of relaxation time and pressure. The curve of pressure *v.* temperature decreases more rapidly below $T_\lambda$ than above, and this is roughly analogous with the behavior of the viscosity in liquid helium, but there is no quantitative similarity. In particular both the heat conductivity and the viscosity are proportional to the relaxation time so that it is impossible to have a decrease in the viscosity and at the same time an increase by many orders of magnitude in the thermal conductivity no matter what anomalies one might postulate in the relaxation time. The ratio of thermal conductivity to viscosity is independent of $\tau_n$, and this is found to have a discontinuity only just twofold at $T_\lambda$; in liquid helium the factor is about $10^5$.

This is the greatest apparent difference between the transport properties of the Bose-Einstein gas and those of liquid helium. This result is quite consistent with the idea[6] that the anomalously high heat conductivity of helium II is due not directly to statistical degeneracy of any form, but to the presence of second sound waves. These waves are believed to be essentially a disturbance of equilibrium between the numerical populations of the lowest state and the excited states, which has been explicitly excluded from the present calculations.

The isothermal heat transport $Q_2$ carried by unit mass flowing under a pressure gradient is calculated from perturbation theory and the result checks with the thermodynamic expression $Q_2=E+PV$. $Q_2$ falls slowly from its classical value $2.5kT$ at high $T$ to a limit $1.28kT_\lambda$ at $T_\lambda$.

Consider two enclosures filled with the same Bose-Einstein gas and connected by a hole so small that no significant perturbations are caused in the velocity distributions of either enclosure. In the presence of the temperature difference $\Delta T$ there will exist a pressure difference $\Delta P$ if no net mass flow is permitted through the hole. The ratio $\Delta P/\Delta T$ is sometimes called the Knudsen pressure coefficient.[7] The Knudsen isothermal heat transfer $Q_1$ is defined as the heat carried per unit mass in a flow due to a pressure difference across the hole but no temperature difference. Both these quantities are found from an ordinary kinetic theory calculation in terms of the Bose Einstein velocity distribution functions, and the results agree with the thermodynamic relation[8]

$$\Delta P/\Delta T=N(Q_2-Q_1)/TV.$$

The heat transfer $Q_1$ goes to zero rather suddenly at $T_\lambda$. This is remarkably like the thermomechanical anomaly in liquid helium flowing through fine slits:[9] it even implies a sudden increase in the Knudsen pressure coefficient, and this may be regarded as a close analogy with the so-called "fountain pressure" effect in helium II.

In the Bose-Einstein gas this effect is due entirely to the statistical degeneracy and has nothing to do with the van der Waals forces. It is due to the fact already stressed, that below $T_\lambda$ the excited particles exert a pressure that is a single valued function of the temperature alone, so that if there is no temperature difference across the small hole there will be no net flow of excited particles either. It is not due to any prevention of the flow of excited particles in either direction, but merely an exact balance of flow in both directions. The only net mass flow will be composed of lowest-state particles, and the only pressure difference will be due to the dependence of the lowest energy levels on their population. The only energy transferred through the hole will be this difference in the lowest energy, and if we go to the limit of perfection in the ideal gas this vanishes; and in any case it is negligible compared with the thermal energy.

In the search for a theory of the peculiar properties of liquid helium we are confronted by the following obvious obstacle: the theory of a quantum liquid could conceivably be derived unambiguously from the theory of classical liquids by means of some form of the correspondence principle, but no really acceptable molecular theory of the classical liquid as yet exists in a form that can be handled with any degree of facility. The attempt to overcome this obstacle and to approach the quantum liquid via the classical liquid may be called the vertical approach. It is well illustrated by the recent work of Born and Green,[10] and also by the present writer's extension of J. E. Mayer's classical statistical thermodynamics of mixed liquids to include the effects of quantum degeneracy.[11]

Another simpler if less rigorous approach is however possible. The problem of the classical liquid has been attacked from the theory of the

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[6] L. Meyer and W. Band, Phys. Rev. **73**, 226 (1948).

[7] M. Knudsen, Ann. d. Physik **34**, 603 (1911); S. Weber, Zeits. f. Physik **24**, 267 (1924).

[8] C. Wagner, Ann. d. Physik **V3**, 629 (1929); L. Onsager, Phys. Rev. **38**, 2265 (1931); R. S. de Groot, Physica **13**, 555 (1947).

[9] L. Meyer and W. Band, Naturwiss., in press (review of the present state of the helium II problem).

[10] M. Born and H. S. Green, Proc. Roy. Soc. **A189**, 103 (1947); **A190**, 455 (1947); **A191**, 108 (1947); **A192**, 166 (1948); and Nature **161**, 391 (1948).

[11] W. Band, J. Chem. Phys. **16**, 343 (1948).

classical solid on the one side, and from the classical gas on the other. Parallel to this attack, we may approach the quantum liquid problem from either side—the quantum solid or the quantum gas. Such a horizontal approach to the quantum liquid was employed in some early work by F. London;[12] it has one significant advantage over the vertical approach: namely that the theories of the quantum gas and the quantum solid are fairly well developed and comparatively elementary, so that the starting point is more easy to handle than for the vertical approach from the classical liquid.

In the present paper we have not attacked the problem of the quantum liquid directly, but have made a preliminary study of the transport properties of the degenerate Bose-Einstein gas in the hope that by so doing we may consolidate the horizontal approach to the quantum liquid. It is at least encouraging that some of the transport properties of the gas are found to be remarkably similar with those of helium II.

## EQUILIBRIUM PROPERTIES OF THE BOSE-EINSTEIN GAS

First approximations to most of the properties of the ideal Bose-Einstein gas can be derived from a smoothed integration over the entire energy spectrum. In this paper we use instead a method similar to that due to F. London[12] in which the lowest energy states are included discretely, and only those states above some arbitrary level treated approximately by integration.

The Gibbs free energy $G=kT\ln\lambda$ is determined by

$$N/V=(4\pi/h^3)\int_{p_1}^{\infty}\{\lambda^{-1}e^{p^2/2mkT}-1\}^{-1}p^2dp$$
$$+\sum_{s=0}^{z}w_s\{\lambda^{-1}e^{\epsilon_s/kT}-1\}^{-1}$$

where $p_1$ is the lowest momentum not included discretely, $\epsilon_s$ is the energy of the $s$th discrete state, $w_s$ the weight per unit volume of the $s$th state, $\epsilon_0$ and $w_0$ belong to the lowest state ($\epsilon_0=0$), and $\epsilon_z$, $w_z$ to the highest state in the discrete spectrum. For the purposes of the present paper it is convenient to express this equation in the form:

$$N/V=(4\pi/h^3)\int_{p_1}^{\infty}p^2\sum_{j=1}^{\infty}\lambda^je^{-jp^2/2mkT}dp$$
$$+\sum_{s=0}^{z}w_s\sum_{j=1}^{\infty}\lambda^je^{-j\epsilon_s/kT}. \quad (1.1)$$

For convenience we shall call the lowest energy states the $s$-states and the states in the integral the $n$-states.

The statistical weight of the discrete state $\epsilon_s$ is the volume in momentum space between the energy levels $\epsilon_s$ and $\epsilon_{s+1}$:

$$w_s=(4\pi/3h^3)\{(2m\epsilon_{s+1})^{\frac{3}{2}}-(2m\epsilon_s)^{\frac{3}{2}}\}$$
$$=(2\pi mkT)^{\frac{3}{2}}h^{-3}(4/3(\pi)^{\frac{1}{2}})\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}. \quad (1.2)$$

The suffix $s+1$ has been used deliberately in the last expression to permit the lowest state to be included formally. To express (1.1) in a form that is more easily handled we need a number of abbreviations and theorems that will be collected here rather than in an appendix, because without seeing them, the reader would find many of the ensuing equations meaningless. The theorems have little intrinsic mathematical importance so their proofs are not given.

Definition:

$$I(n,j)\equiv\frac{2^{n+1}/(\pi)^{\frac{1}{2}}}{1\cdot3\cdot5\cdots(2n-1)}\int_{(j\varphi)^{\frac{1}{2}}}^{\infty}Z^{2n}e^{-Z^2}dZ,$$
$$\varphi\equiv\epsilon_z/kT=p_1{}^2/2mkT. \quad (1.3)$$
$$[n,j=1,2,3,\cdots]$$

$$I(0,j)\equiv(2/(\pi)^{\frac{1}{2}})\int_{(j\varphi)^{\frac{1}{2}}}^{\infty}e^{-Z^2}dZ. \quad (1.4)$$

Theorem:

$$I(n,j)=I(0,j)$$
$$+e^{-j\varphi}\sum_{k=0}^{n-1}\frac{2^{n-k}/(\pi)^{\frac{1}{2}}}{1\cdot3\cdot5\cdots(2n-2k-1)}(j\varphi)^{n-k-\frac{1}{2}}. \quad (1.5)$$

The integrals $I(n,j)$ all approach unity in the limit $p_1\rightarrow0$.

Definitions:

$$\Lambda(n,m)\equiv\sum_{j=1}^{\infty}I(n,j)\lambda^j/j^m, \quad (1.6)$$

$$H(q,m)\equiv\varphi^q\sum_{j=1}^{\infty}e^{-j\varphi}\lambda^j/j^m, \quad (1.7)$$

$$H_s(q,m)\equiv\varphi_s{}^q\sum_{j=1}^{\infty}e^{-j\varphi_s}\lambda^j/j^m,\quad\varphi_s=\epsilon_s/kT. \quad (1.8)$$

Theorems:

The radius of convergence of the $j$-series in $\Lambda(n,m)$ is

$$\lambda=1/(1-\varphi),\ \text{all } n,\ m. \quad (1.9)$$

The series $H_s(q,m)$ all diverge when

$$\lambda\rightarrow e^{\epsilon_s/kT}. \quad (1.10)$$

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[12] F. London, J. Phys. Chem. **43**, 49 (1939); Phys. Rev. **54**, 947 (1938).

The radii of convergence, $e^{\epsilon_s/kT}$ form a monotonically increasing sequence:

$$1=e^{\epsilon_0/kT}<e^{\epsilon_1/kT}<\cdots<e^{\epsilon_z/kT}<1/(1-\varphi). \quad (1.11)$$

The series $H_0(q, m)$ is thus the first to diverge as $\lambda$ increases. The following theorems on the first variations of the $\Lambda$'s and $H$'s are true if $p_1$ is kept constant:

$$\Delta\Lambda(n, m)=\Lambda(n, m-1)\Delta\ln\lambda+\frac{2^n/(\pi)^{\frac{1}{2}}}{1\cdot 3\cdot 5\cdots(2n-1)}$$
$$\times H(n+\tfrac{1}{2}, m-n-\tfrac{1}{2})\Delta\ln T, \quad (1.12)$$

$$\Delta H(q, m)=H(q, m-1)\Delta\ln\lambda+\{qH(q-1, m)$$
$$-H(q, m-1)\}\Delta\ln\varphi, \quad (1.13)$$

$$\Delta H_s(q, m)=H_s(q, m-1)\Delta\ln\lambda+\{qH_s(q-1, m)$$
$$-H_s(q, m-1)\}\Delta\ln\varphi_s. \quad (1.14)$$

Theorem:

$$\Lambda(n, m)=\Lambda(n-1, m)+\frac{2^n/(\pi)^{\frac{1}{2}}}{1\cdot 3\cdot 5\cdots(2n-1)}$$
$$\times H(n-\tfrac{1}{2}, m-n+\tfrac{1}{2}). \quad (1.15)$$

In terms of the foregoing notation we now write (1.1) in the form:

$$N/V=(2\pi mkT)^{\frac{3}{2}}h^{-3}\left\{\Lambda(1, \tfrac{3}{2})+\sum_{s=0}^{z}(4/3(\pi)^{\frac{1}{2}})\right.$$
$$\left.\times\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}H_s(0, 0)\right\}. \quad (1.16)$$

The lambda-transition occurs at that temperature which forces $\lambda$ to approach the smallest of the radii of convergence: namely the value unity that makes the series $H_0(0, 0)$ diverge.

The individual terms in the $s$-sum of (1.16) are generally exceedingly small compared with the leading $\Lambda$-term; they represent the populations of the individual discrete states, whereas the $\Lambda$-term represents the integral (or sum) over all the $n$-states. As soon as the value of $\lambda$ is close enough to unity the population of the lowest state begins to increase, and because when $\lambda=1$, $H_0(0, 0)$ actually diverges, there is no limit to the population of this state. However $\lambda$ has to be so close to unity to make $H_0(0, 0)$ comparable with the $\Lambda$ term, that we can write $\lambda=1$ in all the other terms in (1.16) in order to estimate the transition temperature. This temperature, $T_\lambda$ is therefore given by

$$N/V=(2\pi mkT_\lambda)^{\frac{3}{2}}h^{-3}\left\{\Lambda_c(1, \tfrac{3}{2})+\sum_{s=1}^{z}(4/3(\pi)^{\frac{1}{2}})\right.$$
$$\left.\times\Delta(\epsilon_{s+1}/kT_\lambda)^{\frac{3}{2}}H_{sc}(0, 0)\right\}, \quad (1.17)$$

where the $s=0$ term is absent, and $\Lambda_c(1, \frac{3}{2})$ and $H_{sc}(0, 0)$ denote the values at $\lambda=1$. When $T$ goes below $T_\lambda$ the right hand side of (1.17) decreases, and the deficiency is made up by the divergent $H_0$ term.

In (1.17) the $s$-sum actually makes only a small correction to the calculation of $T_\lambda$, and it is sufficient to evaluate it to a first approximation. If we agree to keep $\epsilon_z/kT\ll 1$, we have

$$H_{sc}(0, 0)=\sum_{j=1}^{\infty}e^{-j\epsilon_s/kT}\doteq kT/\epsilon_s. \quad (1.18)$$

To the same approximation the $s$-sum in (1.17) becomes

$$(4/3(\pi)^{\frac{1}{2}})\sum_{s=1}^{z}(kT/\epsilon_s)\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}$$
$$\doteq(2/(\pi)^{\frac{1}{2}})\sum_{s=1}^{z}(kT\epsilon_s)^{-\frac{1}{2}}\Delta\epsilon_s$$
$$=(4/(\pi)^{\frac{1}{2}})\{(\epsilon_z/kT)^{\frac{1}{2}}-(\epsilon_1/kT)^{\frac{1}{2}}\}. \quad (1.19)$$

The strict requirement for the accuracy of this result is thus

$$(\epsilon_z/kT)^{\frac{1}{2}}\ll 1. \quad (1.20)$$

On this understanding the transition temperature is determined by

$$N/V=(2\pi mkT_\lambda)^{\frac{3}{2}}h^{-3}$$
$$\times\{\Lambda_c(1, \tfrac{3}{2})+(4/(\pi)^{\frac{1}{2}})(\epsilon_z/kT)^{\frac{1}{2}}\}. \quad (1.21)$$

Now the quantity $\epsilon_z$ is entirely arbitrary, and it is clear that the correct value of $T_\lambda$ should be independent of the choice of this parameter. The approximation (1.18) will therefore presumably be acceptable if the parameter can be so chosen that $T_\lambda$ has a stationary value with respect to variations of $\epsilon_z$, all other quantities remaining fixed.

Using the definitions (1.3), (1.4), (1.6) and the theorem (1.5) we can write the bracketed expression on the right hand side of (1.21) in the form:

$$\sum_{j=1}^{\infty}\{1-P((j\varphi)^{\frac{1}{2}})+(2/(\pi)^{\frac{1}{2}})(j\varphi)^{\frac{1}{2}}e^{-j\varphi}\}j^{-\frac{3}{2}}$$
$$+(4/(\pi)^{\frac{1}{2}})\varphi^{\frac{1}{2}}\equiv F(\varphi), \quad (1.22)$$

where $P(x)$ is the probability integral normalized to unity. Differentiating this with respect to $\varphi$ we find, if $\varphi$ is small

$$\partial F/\partial\varphi=(\varphi/\pi)^{\frac{1}{2}}. \quad (1.23)$$

This is positive and vanishes only at $\varphi=0$, but $\varphi\partial F/\partial\varphi$ remains small compared with $\varphi$ for small $\varphi$. Thus any choice of $\varphi$ conforming to (1.20) is such that there is no appreciable dependence of $T_\lambda$ on $\varphi$.

Choosing for example $\varphi=0.01$ we have evaluated $F(\varphi)$ exactly by direct summation and compared with the result given by integration approximation ($\varphi=0$). We find

$$F(0.01)=2.616, \quad F(0)=2.612. \tag{1.24}$$

The modification in $T_\lambda$ due to this second approximation is therefore less than 0.2 percent.* Implicit in this calculation is the assumption that the volume $V$ of the gas is large enough to ensure the presence of a considerable number (say ten or more) of energy levels in the range $0.01kT$. In fact the volume has to be less than about $10^{-16}$ cc before this condition would be formally violated!

We conclude that for the ideal gas the integration approximation gives sufficiently precise values for the transport properties: their computation generally involves series that converge more rapidly than those involved in the evaluation of $T_\lambda$. The numerical results given in the present paper have been calculated only on this approximation, but the formal analysis has been carried through in terms of the second approximation because it will later enable us to study the properties of special models in which any desired anomalies may be present in the lower energy levels.

Below the transition temperature $T_\lambda$ the number of particles $N_n$ in the $n$-states is given by

$$N_n/V=(2\pi mkT)^{\frac{3}{2}}h^{-3}\Lambda_c(1, \tfrac{3}{2}) \tag{1.25}$$

and the total number of particles in the $s$-states is the difference

$$\sum_{s=0}^{z} N_s/V=N/V-N_n/V. \tag{1.26}$$

However the number in the lowest state alone has to be found from a more precise calculation of the $s$-sums in (1.17). Provided we keep close enough to the transition temperature to allow (1.20) to remain valid, we may use (1.21) instead of (1.17) and write

$$\begin{aligned} N_0/V=N/V-(2\pi mkT)^{\frac{3}{2}}h^{-3} \\ \times\{\Lambda_c(1, \tfrac{3}{2})+4/(\pi)^{\frac{1}{2}})(\epsilon_z/kT)^{\frac{1}{2}}\} \end{aligned} \tag{1.27}$$

Because both $\Lambda_c(1, \frac{3}{2})$ and $\epsilon_z/kT$ depend on $T$ below $T_\lambda$, this equation is not exactly of the same form as that given by the integration approximation, namely:

$$N_0/V=(N/V)\{1-(T/T_\lambda)^{\frac{3}{2}}\}$$

But because the $T$-variation of the expression in {brackets} in (1.27) is essentially proportional to its $\varphi$-variation, and because we have chosen $\varphi$ at $T_\lambda$ so that the $\varphi$-variation is almost zero, we may assume also that at least near to $T_\lambda$ its $T$-variation is also almost zero. Hence the two expressions for $N_0$ almost coincide.

The total energy $E_n$ of the particles in the $n$-states is given by

$$E_n/V=(3/2)kT(2\pi mkT)^{\frac{3}{2}}h^{-3}\Lambda(2, 5/2), \tag{1.28}$$

while the energy in any one of the $s$-states is given by

$$E_s/V=w_s kTH_s(1, 0). \tag{1.29}$$

The general relation $P=2E/3V$ is still true here, and we can immediately write down the partial pressures due respectively to the $n$-particles and to each of the $s$-states:

$$\begin{aligned} P_n&=kT(2\pi mkT)^{\frac{3}{2}}h^{-3}\Lambda(2, 5/2) \\ P_s&=(2/3)kTw_sH_s(1, 0), \end{aligned} \tag{1.30}$$

and obtain the total pressure exerted by the gas:

$$P=kT(2\pi mkT)^{\frac{3}{2}}h^{-3}\left\{\Lambda(2, 5/2)+\sum_{s=0}^{z}(8/9(\pi)^{\frac{1}{2}}) \times\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}H_s(1, 0)\right\}. \tag{1.31}$$

Using (1.16) we then find the equation of state in the more convenient form:

$$PV=NkT\frac{\Lambda(2, 5/2)+\sum_{s=0}^{z} (8/9(\pi)^{\frac{1}{2}})\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}H_s(1, 0)}{\Lambda(1, 3/2)+\sum_{s=0}^{z} (4/3(\pi)^{\frac{1}{2}})\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}H_s(0, 0)}. \tag{1.32}$$

Going over to the integration approximation we find

$$\begin{aligned} &T\leqslant T_\lambda, &P&=\zeta(5/2)kT(2\pi mkT)^{\frac{3}{2}}h^{-3}, \\ &T=T_\lambda, &P&=\zeta(5/2)kT_\lambda(2\pi mkT_\lambda)^{\frac{3}{2}}h^{-3}, \\ &T\geqslant T_\lambda, &P/P_\lambda&=(T/T_\lambda)\zeta(3/2)\zeta(\lambda, 5/2) \\ &&&\quad\div\zeta(\lambda, 3/2)\zeta(1, 5/2), \end{aligned}$$

where $\zeta(n)$ is the Riemann zeta-function

$$\sum_{j=1}^{\infty} 1/j^n$$

and $\zeta(\lambda, n)$ is an "incomplete" Reimann zeta-

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* This discussion of the lambda-point differs essentially from that given by F. London and referred to above. In his treatment the discrete set of states was lumped together and the $s$-sum of our expression (1.1) was represented only by a single term in which the mean energy of the particles in the discrete states appeared in the exponent. The radius of divergence of this series was therefore $e^{\bar{\epsilon}_s/kT}$ where $\bar{\epsilon}_s$ was the mean energy of the $s$-particles. London used a constant value for this mean energy $\bar{\epsilon}_s=3\epsilon_s/5$ where $\epsilon_s$ was the energy of the lowest state in the integral, or the highest discrete state. This would be correct only at high temperatures, but near the lambda-point the mean energy drops towards zero. London's calculation would lead to a value of $T_\lambda$ appreciably different from the result of the integration approximation even for the ideal gas.

function:

$$\zeta(\lambda, n) \equiv \sum_{j=1}^{\infty} \lambda^j / j^n.$$

These are limiting forms of the $\Lambda$ functions when $\varphi$ is zero.

Figure 1 shows the temperature dependence of the parameter $\lambda$ on the integration approximation, and Fig. 2 shows the pressure curves for several arbitrary values of $T_\lambda$, calculated for a gas with atoms equal in mass to those of He$^4$.

### FIRST-ORDER PERTURBATION THEORY

The unperturbed distribution function giving the number of $n$-particles per unit volume in a cell $dv_x dv_y dv_z$ of velocity space (see Eq. (1.1)) is

$$f_{n0}(v)dv_x dv_y dv_z = (m/h)^3 \sum_{j=1}^{\infty} \lambda^j e^{-jmv^2/2kT} dv_x dv_y dv_z. \quad (2.1)$$

The unperturbed distribution function for particles in each $s$-state gives the number of particles per unit volume per unit solid angle:

$$f_{s0}(v)d\Omega = w_s H_s(0, 0)d\Omega, \quad d\Omega = \sin\theta d\theta d\Phi/4\pi. \quad (2.2)$$

The first function applies to all velocities $v \geqslant p_1/m$ while the others apply only to the particular velocities $v_s$, respectively, the magnitudes $v_s$ being constant in each function.

Consider the perturbations that leave the energy levels unchanged but which are of such a form that the functions become

$$\left.\begin{aligned} f_n(v) &= f_{n0}(v) + f_{n1}(v) \\ \text{where} \quad f_{n1}(v) &= -\tau_n v_x \partial f_{n0}(v)/\partial x \end{aligned}\right\} \quad (2.3)$$

and

$$\left.\begin{aligned} f_s(v) &= f_{s0}(v) + f_{s1}(v) \\ \text{where} \quad f_{s1} &= -\tau_s v_{sx} \partial f_{s0}(v)/\partial x \end{aligned}\right\} \quad (2.4)$$

$$s = 1, 2, 3 \cdots z.$$

In (2.3) $v_x = v\cos\theta$, while in (2.4) $v$ has the magnitude $v_s = (2\epsilon_s/m)^{\frac{1}{2}}$ and $v_{sx} = v_x \cos\theta$.

These are Boltzmann type perturbation equations and involve no changes in the equilibrium populations of any given energy range or in any given discrete level. $\tau_n$ and $\tau_s$ are relaxation times for the readjustment of equilibrium in the spherical symmetry of the velocity distributions. One would like to be able to compute these times from a complete theory of collision probabilities between the atoms. However such a calculation could hardly be free of speculative elements specially with regard to the collision cross sections attributable to the particles condensed into the lowest energy level. Fortunately, the formal theory can be developed without such a calculation, the results being expressible in terms of the relaxation times as unknown parameters. For notational symmetry we retain all the $\tau_s$ as distinct, but eventually only $\tau_0$ for the lowest state will be considered as possibly different from the others.

It will further be supposed that the relaxation times are long compared with the relaxation time, which must also exist in principle, for adjustment of equilibrium between the relative numerical populations of the various states: in other words all the perturbation functions contain the same value of the equilibrium parameter $\lambda$ at any given point in space.

This last assumption may in fact be invalid below the lambda-point, according to ideas developed elsewhere:[5] the transition probabilities between particles in the lowest state and those in the excited states may become so low as to cause trouble. We shall not consider this kind of complication in the present paper.

Using the above perturbed distribution functions we obtain for the net flow of particles per second

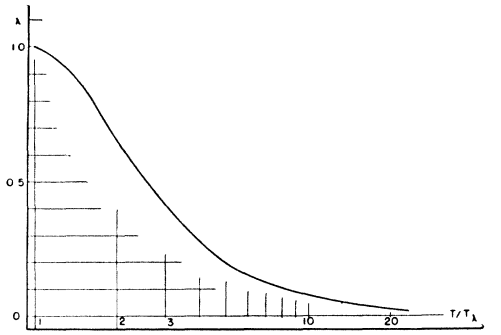

FIG. 1. The temperature dependence of the statistical parameter $\lambda$ calculated on the integration approximation.

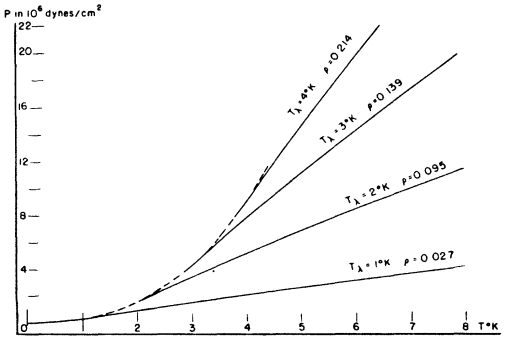

FIG. 2. The pressure-temperature curves for several arbitrary densities calculated for a gas with atoms equal in mass to those of He$^4$.

across unit area in $x$-direction:

$$J = {}^{*}\int_{-\infty}^{\infty}\!\!\int\!\!\int{}^{*}\, v\cos\theta f_{n1}(v)\,dv_x dv_y dv_z$$

$$+\sum_{s=0}^{z}\int_{\theta=0}^{\pi}\int_{\Phi=0}^{2\pi} v_s\cos\theta f_{s1}(v)\,d\Omega, \quad (2.5)$$

where the integral sign $*\int\int\int*$ is intended to indicate that the integration is to be taken only over the region in velocity space *outside* of the sphere of radius $v_z=(2\epsilon_z/m)^{\frac{1}{2}}$. To handle this and similar integrals we use the following additional theorem:

$$ {}^{*}\int_{-\infty}^{\infty}\!\!\int\!\!\int{}^{*}\, v_x{}^2 v^{2n}\sum_{j=1}^{\infty} j\lambda^j e^{-jmv^2/2kT}dv_x dv_y dv_z$$

$$=(4/3)(\pi)^{\frac{3}{2}}(2kT/m)^{n+5/2}\left\{\frac{1\cdot3\cdot5\cdots(2n+3)}{2^{n+3}}\right\}$$

$$\times\sum_{j=1}^{\infty} I(n+2,\, j)\lambda^j/j^{n+\frac{3}{2}}. \quad (2.6)$$

This theorem permits (2.5) to be written out:

$$J=-\tau_n(kT/m)(2\pi mkT)^{\frac{3}{2}}h^{-3}$$

$$\times\{\Lambda(2,\,3/2)d\ln\lambda/dx$$

$$+(5/2)\Lambda(3,\,5/2)d\ln T/dx\}$$

$$-\sum_{s=0}^{z}(2\tau_s/3)(kT/m)w_s H_s(1,\,-1)$$

$$\times\{d\ln\lambda/dx-d\ln\varphi_s/dx\}. \quad (2.7)$$

The net flow of energy per second across unit area is similarly

$$W={}^{*}\int_{-\infty}^{\infty}\!\!\int\!\!\int{}^{*}\,\tfrac{1}{2}mv^2 v\cos\theta f_{n1}(v)\,dv_x dv_y dv_z$$

$$+\sum_{s=0}^{z}\int_{\theta=0}^{\pi}\int_{\Phi=0}^{2\pi}\epsilon_s v_s\cos\theta f_{s1}(v)\,d\Omega \quad (2.8)$$

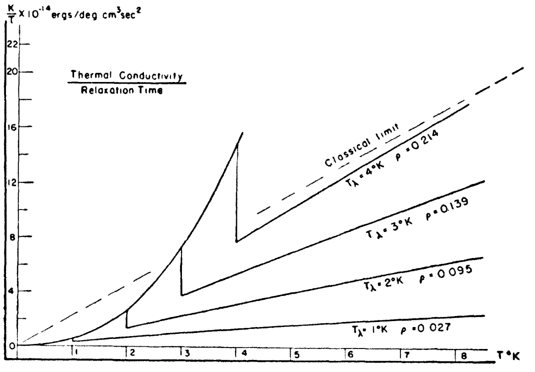

FIG. 3. Thermal conductivity curves for a gas with atoms equal in mass to those of He⁴.

and again using (2.6) this can be written in the form:

$$W=-(\tau_n/m)(kT)^2(2\pi mkT)^{\frac{3}{2}}h^{-3}$$

$$\times\{(5/2)\Lambda(3,\,5/2)d\ln\lambda/dx$$

$$+(35/4)\Lambda(4,\,7/2)d\ln T/dx\}$$

$$-\sum_{s=1}^{z}(2/3)(\tau_s/m)(kT)^2 w_s H_s(2,\,-1)$$

$$\times\{d\ln\lambda/dx-d\ln\varphi_s/dx\}. \quad (2.9)$$

Expressed in terms of the temperature gradient, we may write (2.9) as

$$W=-(d\ln T/dx)(\tau_n/m)(kT)^2(2\pi mkT)^{\frac{3}{2}}h^{-3}$$

$$\times\Bigg[\Bigg\{(5/2)\Lambda(3,\,5/2)+\sum_{s=0}^{z}(8/9(\pi)^{\frac{1}{2}})(\tau_s/\tau_n)$$

$$\times\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}H_s(2,\,-1)\Bigg\}\Bigg\}d\ln\lambda/d\ln T$$

$$+\Bigg\{(35/4)\Lambda(4,\,7/2)+\sum_{s=0}^{z}(8/9(\pi)^{\frac{1}{2}})$$

$$\times(\tau_s/\tau_n)\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}H_s(2,\,-1)\Bigg\}\Bigg]. \quad (2.10)$$

The thermal conductivity is to be measured in the absence of any net mass flow, and this condition, namely $J=0$, used in (2.7) determines the variation of $\ln\lambda$. Thus:

$$J=0,\quad d\ln\lambda/d\ln T=-\frac{(5/2)\Lambda(3,\,5/2)+\sum_{s=0}^{z}(8/9(\pi)^{\frac{1}{2}})(\tau_s/\tau_n)\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}H_s(1,\,-1)}{\Lambda(2,\,3/2)+\sum_{s=0}^{z}(8/9(\pi)^{\frac{1}{2}})(\tau_s/\tau_n)\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}H_s(1,\,-1)}. \quad (2.11)$$

At sufficiently high temperatures (2.11) reduces to 5/2 and the thermal conductivity becomes:

$$T\gg T_\lambda,\quad K=W\div dT/dx$$

$$=-(5/2)(\tau_n/m)(N/V)k^2T.$$

Generally on the integration approximation we find

$$T\geqslant T_\lambda,\quad K=-(5/4)(k^2T/m)(N/V)$$

$$\times[7\zeta(\lambda,\,7/2)/\zeta(\lambda,\,3/2)$$

$$-5\{\zeta(\lambda,\,5/2)/\zeta(\lambda,\,3/2)\}^2]. \quad (2.12)$$

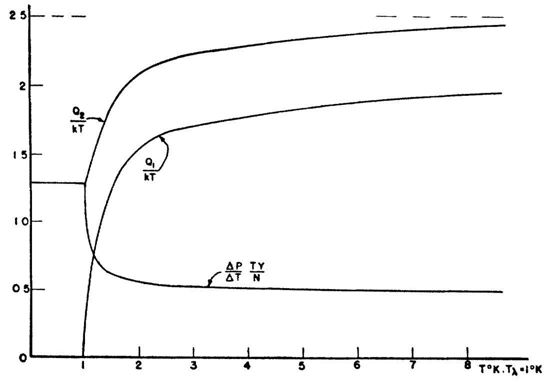

FIG. 4. The heat content, the Knudsen isothermal heat of transport, and the Knudsen pressure coefficient in units of $kT$ plotted against $T/T_\lambda$.

Below $T_\lambda$ we run into the difficulty that $\Delta \ln\lambda$ must remain zero and it is actually impossible to satisfy (2.11). In other words Eq. (1.31) leads to a pressure that is a single valued function of $T$ only below $T_\lambda$, and a decrease of volume or an increase of density can only result in increasing the density of the population in the lowest state, and these do not contribute to the pressure. Physically we have to suppose that the mass flow given by (2.7) can actually be balanced by a return current of particles in the lowest state, although this cannot appear in the formal analysis. On this understanding we can still define a conductivity below $T_\lambda$, and putting $\Delta \ln\lambda = 0$ in (2.9) we find

$$T \leqslant T_\lambda, \quad K = -(35/4)(\tau_n/m)(N_n/V)k^2T \times \Lambda_c(4, 7/2)/\Lambda_c(1, 3/2). \tag{2.13}$$

There is thus apparently a discontinuity of the conductivity by a factor of almost 2 as $T$ drops through the transition temperature. Figure 3 shows the curves drawn from the integration approximation.

As discussed in the Introduction, nothing like superconductivity for heat is to be expected in the ideal gas.

The isothermal heat transport accompanying mass flow is derived from (2.9) by writing $\Delta T = 0$ and dividing the result by the value of $J$ obtained from (2.7) also with $\Delta T = 0$. The result is

$$Q_z \equiv (W/J)_{T=\text{const.}} = kT\frac{(5/2)\Lambda(3, 5/2) + \sum_{s=0}^{z}(8/9(\pi)^{\frac{1}{2}})(\tau_s/\tau_n)\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}H_s(2, -1)}{\Lambda(2, 3/2) + \sum_{s=0}^{z}(8/9(\pi)^{\frac{1}{2}})(\tau_s/\tau_n)\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}H_s(1, -1)} \tag{2.14}$$

or on the integration approximation

$$Q_2 = 5kT\zeta(\lambda, 5/2)/2\zeta(\lambda, 3/2). \tag{2.15}$$

This curve is shown on Fig. 4. At very high temperatures it coincides with the classical result $Q_2 = 5kT/2$.

If (1.28), (1.29) and (1.31) are used with the approximation (1.18) and (1.19) in (2.14) we arrive at the thermodynamic relation

$$NQ_2/V = E/V + P. \tag{2.16}$$

There is no marked discontinuity in $Q_2$ at $T_\lambda$.

From the same perturbation theory we can compute the viscosity of the gas. We set up the unperturbed distribution functions in the form

$$\begin{aligned} f_{n0}(v) &= (m/h)^3 \sum_{j=1}^{\infty} \lambda^j \exp[-jm(\mathbf{v}+\mathbf{u})^2/2kT], \\ f_{s0}(v) &= w_s \sum_{j=1}^{\infty} \lambda^j \exp[-jm(\mathbf{v}_s+\mathbf{u})^2/kT], \\ & \qquad s = 0, 1, \cdots z, \end{aligned} \tag{2.17}$$

where $\mathbf{u}$ means the speed of flow of the gas at a distance $y$ from the wall, and $\mathbf{v}$ is the velocity of the particle relative to stationary coordinates. We allow $u$ to depend on $y$ so that $\partial u/\partial y$ is a constant. We then allow perturbations such that

$$\left.\begin{aligned} & f_n(v) = f_{n0}(v) + f_{n1}(v) \\ \text{where} \quad & \\ & f_{n1}(v) = -\tau_n v_y \partial f_{n0}(v)/\partial y. \end{aligned}\right\} \tag{2.18}$$

We then find the flow of $x$-momentum across a surface normal to the $y$-direction, and this finally gives the coefficient of viscosity as the ratio of the momentum transfer to the velocity gradient

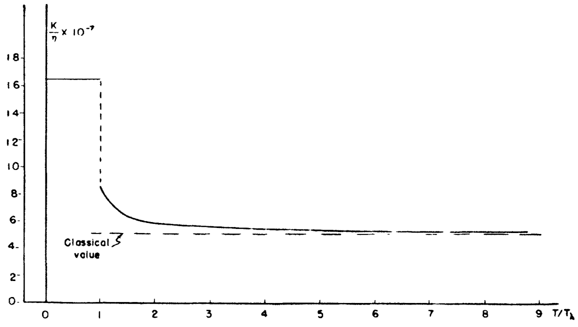

FIG. 5. The ratio of thermal conductivity to viscosity as a function of $T/T_\lambda$.

$\partial u/\partial y$. The result turns out to be

$$\eta=\tau_n P_n \Lambda(3,\,5/2)/\Lambda(2,\,5/2) +\sum_{s=0}^{z}\tau_s P_s(\epsilon_s/kT). \quad (2.19)$$

We note specially that the lowest state contributes nothing to the viscosity because it exerts no pressure. At high temperatures (2.19) reduces to the simple result:

$$T\gg T_\lambda, \quad \eta=\tau_n P. \quad (2.20)$$

This agrees with the classical kinetic theory if we use the classical expression for the mean free path and mean speed with which to express the relaxation time. Generally the integration approximation gives

$$T\geqslant T_\lambda \text{ and } T<T_\lambda, \quad \eta=\tau_n P \quad (2.21)$$

a result which holds for all temperatures.

The most significant consequence of these calculations is obtained by taking the ratio between $K$ and $\eta$, because this is independent of $\tau$. Figure 5 shows the curve. There is a discontinuity of about two-fold at $T_\lambda$, but $K/\eta$ remains finite below $T_\lambda$ so that it is clear that no assumed anomaly in $\tau_n$ at $T_\lambda$ could give both superfluidity and superconductivity for heat below the transition temperature.

## THE KNUDSEN PHENOMENA

Exclude from the range of integration the region of momentum space in which the total momentum is less than $p_1$ so that

$$p_x^2+p^2\geqslant p_1^2 \quad \text{where} \quad p^2\equiv p_y^2+p_z^2. \quad (3.1)$$

The number of $n$-particles with $x$-momentum within the range $p_x$ to $p_x+dp_x$ incident per second on unit area normal to the $x$-axis is

$$n(p_x)dp_x=(\pi/3m)p_x dp_x\int_\rho^\infty \sum_{j=1}^{\infty}\lambda^j \times e^{-j(p^2+p_x^2)/2mkT}dp^2, \quad (3.2)$$

where

$$\left.\begin{aligned} &\rho^2=p_1^2-p_x^2 \quad \text{if} \quad |p_x|<|p_1| \\ \text{or} \quad &\rho^2=0 \quad \text{if} \quad |p_x|\geqslant|p_1|. \end{aligned}\right\}. \quad (3.3)$$

This integral can be written in the form

$$n(_n\equiv\int_0^\infty n(p_x)dp_x=2\pi m(kT)^2h^{-3} \times\{H(0,\,2)+H(1,\,1)\} \quad (3.4)$$

and equals the total number of $n$-particles striking unit area per second.

Assuming spherical isotropy of the velocity distribution in each $s$-state, it is easy to calculate the number of such particles striking unit area:

$$n(_s=\tfrac{1}{4}(N_s/V)(p_s/m)=\tfrac{1}{4}w_s(2kT/m)^{\frac{1}{2}}H_s(\tfrac{1}{2},\,0). \quad (3.5)$$

The pressure exerted by the gas can be obtained from these by integrating expressions like $2p_x$ times (3.2). The results confirm Eq. (1.30). The kinetic energy carried by the particles arriving per second per unit area is found by integrating the expression, for the $n$-states:

$$\epsilon(_n=\int(1/2m)(p^2+p_x^2)n(p_x)dp_x. \quad (3.6)$$

The result is

$$\epsilon(_n=4\pi m(kT)^3h^{-3} \times\{H(0,\,3)+H(1,\,2)+\tfrac{1}{2}H(2,\,1)\}. \quad (3.7)$$

For the $s$-states, where each $s$-particle carries the same energy for any given value of $s$, we find the energy arriving per second per unit area:

$$\epsilon(_s=\tfrac{1}{2}w_s(1/2m)^{\frac{1}{2}}(kT)^3H_s(\tfrac{3}{2},\,0). \quad (3.8)$$

To obtain the Knudsen phenomena, consider two enclosures filled with the gas at slightly different pressures and temperatures, and connected by a hole so small that no appreciable disturbance in the mean velocity distribution of the gas occurs in either enclosure in the immediate neighborhood of the hole. The net mass flow through such a hole is its area multiplied by the first variation of the number

$$n(\equiv n(_n+\sum_{s=0}^{z}n(_s. \quad (3.9)$$

The condition for a steady state, zero net mass flow, is

$$\Delta n(=0. \quad (3.10)$$

Put this condition in (3.4), (3.5) and (3.9) and find the following value for the variation of $\ln\lambda$ as between the two enclosures:

$$\frac{\Delta\ln\lambda}{\Delta\ln T}=-\frac{2H(0,\,2)+2H(1,\,1)+H(2,\,0)+\sum_{s=0}^{z}(2/3)\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}H_s(\tfrac{3}{2},\,-1)}{H(0,\,1)+H(1,\,0)+\sum_{s=0}^{z}(2/3)\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}H_s(\tfrac{1}{2},\,-1)}. \quad (3.11)$$

We next write out the first variation of the pressure (1.31) and use the theorems (1.12) to (1.14). Then obtain the pressure difference between the two enclosures required to prevent a net mass flow under the temperature difference $\Delta T$, by using (3.11) in the first variation of the pressure. The result is the Knudsen pressure coefficient:

$$V\Delta P/Nk\Delta T=\frac{\Lambda(2,\tfrac{3}{2})+\sum_{s=0}^{z}(8/9(\pi)^{\frac{1}{2}})\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}H_s(1,-1)}{\Lambda(1,\tfrac{3}{2})+\sum_{s=0}^{z}(4/3(\pi)^{\frac{1}{2}})\Delta(\epsilon_{s+1}/kT)^{\frac{1}{2}}H_s(0,0)}\,\frac{\Delta\ln\lambda}{\Delta\ln T}$$
$$+\frac{(5/2)\Lambda(3,5/2)+\sum_{s=0}^{z}(8/9(\pi)^{\frac{1}{2}})\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}\{H_s(0,0)-H_s(1,-1)+H_s(1,0)\}}{(5/2)\Lambda(3,5/2)+\sum_{s=0}^{z}(8/9(\pi)^{\frac{1}{2}})\Delta(\epsilon_{s+1}/kT)^{\frac{3}{2}}H_s(2,-1)}Q_2.\quad(3.12)$$

At sufficiently high temperatures most of the terms in this expression become negligible and we find the classical result:

$$T\gg T_\lambda,\quad \Delta P/\Delta T=(Nk/V)(5/2-2)=\tfrac{1}{2}Nk/V.\quad(3.13)$$

On the integration approximation

$$H(0,m)=\zeta(\lambda,m)$$

while $H(n,m)=0$, $n\neq 0$. Therefore in place of (3.11) we have

$$\Delta\ln\lambda/\Delta\ln T=-2\zeta(\lambda,2)/\zeta(\lambda,1)\quad(3.11a)$$

while the Knudsen pressure coefficient becomes

$$V\Delta P/Nk\Delta T=5Q_2/2-2\zeta(\lambda,2)/\zeta(\lambda,1).\quad(3.12a)$$

The isothermal Knudsen heat transfer is obtained from the isothermal variation of the energy flow

$$\epsilon(\equiv\epsilon(_n+\sum_{s=0}^{z}\epsilon(_s.\quad(3.14)$$

We use (3.7) and (3.8) and divide the result by the isothermal first variation of $n($ given by (3.9) to obtain the mean energy per particle flowing on average across the hole when there is a pressure difference but no temperature difference. This is the isothermal Knudsen heat transfer $Q_1$ and we find that

$$Q_1/kT \text{ is exactly equal to } -\Delta\ln\lambda/\Delta\ln T$$

as given by the expression (3.11). We may write this on the integration approximation:

$$Q_1/kT=2\zeta(\lambda,2)/\zeta(\lambda,1).\quad(3.15)$$

The curve in Fig. 4 is drawn from this equation. It has the classical value 2 at sufficiently high temperatures.

From quasi-thermodynamics it is expected that

$$V\Delta P/Nk\Delta T=(Q_2-Q_1)/kT\quad(3.16)$$

and it is obvious that the integration approximation, represented by (2.15), (3.12a) and (3.15) that this relation is identically satisfied. If we use the more exact expressions, and accept the same approximation as in (1.18) for evaluating the corrections, we easily confirm that (3.16) is again satisfied.

The actual value of $Q_1$ given by (3.15) is of considerable interest. The denominator becomes infinite at $T_\lambda$ and remains infinite at lower temperatures, so that the heat transferred through the small hole vanishes there. The same result follows on the second approximation. Inspecting (3.11), which yields this second approximation for $Q_1$, we note that the series

$$H(2,0)\quad\text{and}\quad\sum_{s=0}^{z}w_sH_s(\tfrac{3}{2},-1)$$

become the dominant terms in the numerator, while the series

$$H(1,0)\quad\text{and}\quad\sum_{s=0}^{z}w_sH_s(\tfrac{1}{2},-1)$$

are the dominant terms in the denominator. The ratio of these terms is not greater than $\epsilon_z/kT$, and in fact equals the mean energy of the lowest states divided by $kT$, when $T\leqslant T_\lambda$. The mean energy vanishes at and below the lambda-point, because of the greatly increased population of the lowest state, so that again we obtain the same result: *the Bose-Einstein gas cannot transport heat during isothermal flow through a small hole at temperatures below the lambda transition.*

The writer is happy to express his gratitude to Dr. Lothar Meyer, Dr. J. W. Stout, and Dr. Lester Guttman for numerous discussions.