

## Variation in Positron Lifetime with Pressure

R. K. WILSON, P. O. JOHNSON, AND R. STUMP

*Department of Physics and Astronomy, University of Kansas, Lawrence, Kansas*

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The mean life of the long-lived component of positrons annihilating in various solids and liquids has been measured at pressures up to 6000 atm and temperatures up to 200°C. At fixed temperature, the mean life decreases exponentially with the change in volume due to increasing pressure. At fixed volume, the lifetime decreases with increasing temperature. A qualitative explanation of the variation is presented.

### INTRODUCTION

IT has been known for some time<sup>1,2</sup> that positrons stopping in dense materials are annihilated with three characteristic lifetimes. This phenomenon is attributed to the formation of positronium. Positronium formed in the singlet state undergoes two quantum annihilation with a mean life of about  $1.25 \times 10^{-10}$  sec. Positrons which do not form positronium undergo annihilation with electrons of the surrounding material with a mean life which is proportional to the density. For most solids and liquids this lifetime is of the order of  $2 \times 10^{-10}$  sec. The two lifetimes are generally not resolved and are lumped together as a mean life  $\tau_1$  with intensity  $I_1$ . In gases and in liquid helium these two mean lifetimes are easily separated.<sup>3,4</sup> Positrons forming positronium in the triplet state have a mean life longer by an order of magnitude than free positrons. This component has intensity  $I_2$  and mean life  $\tau_2$ .

The positron in triplet (ortho-) positronium may annihilate in three ways. It may combine with the electron of the positronium in three quantum annihilation. The rate for this process is quite low,  $7 \times 10^6$  sec<sup>-1</sup>, so that except in gases (and liquid helium) three quantum annihilation has only a very minor effect on the mean life  $\tau_2$ . If paramagnetic ions, or unpaired electrons, are present, then triplet to singlet conversion of the positronium may occur, followed by two quantum annihilation from the singlet state. Finally, the positron in positronium may annihilate with an electron of the surrounding medium.<sup>5</sup> This process, electron pickoff, is the main mode of annihilation in the work reported here. The pickoff rate obviously depends on the density of the surrounding matter, or, more precisely, on the density at the positron of the wave functions of electrons of the surrounding material.

Bell and Graham<sup>1</sup> observed that the mean life of the  $\tau_2$  component depended strongly on the temperature in most materials. It has been suggested<sup>6-8</sup> that the variation of  $\tau_2$  with temperature is a density effect,

since a change in density due to temperature causes a change in mean life similar to that caused by an equal change in density due to pressure. However, the conclusion that the variation of the mean life  $\tau_2$  with temperature is *entirely* a volume effect is inconsistent with the observations of  $\tau_2$  in liquid and gaseous helium.<sup>9</sup> Likewise, the behavior of both the mean life and the angular correlation of the annihilation radiation shows an anomalous behavior at the ice-water transition.<sup>7,8</sup>

The present work is a further investigation of the annihilation of positronium in liquids and solids at very high pressure in order to separate the effects of temperature and pressure.

### EXPERIMENTAL METHODS

Positrons were obtained from the radioactive decay of Na<sup>22</sup>. The origin of a positron was indicated by the subsequent nuclear  $\gamma$  ray. The annihilation of the positron was indicated by the annihilation quanta. Scintillation counters using plastic scintillators detected the two  $\gamma$  rays. A time-to-pulse-height converter changed the time interval to a pulse height. Single-channel pulse-height analyzers and a slow coincidence circuit were arranged to give a coincidence output only when one counter detected a nuclear  $\gamma$  ray and the other an annihilation  $\gamma$  ray. The slow coincidence output gated the time-to-pulse-height converter output. The resulting pulses were analyzed on an RCL 256-channel pulse-height analyzer.

The liquid samples were prepared by evaporating to dryness a solution of Na<sup>22</sup>Cl in a stainless-steel cup, then filling the cup with the liquid to be investigated. The cup was then inverted into a larger cup containing mercury which formed the seal between the pressure-transmitting oil and the liquid under test. The dimensions of the sample were limited by the requirement that the walls of the pressure system be thin enough to allow most of the gamma rays to pass. As a result, about 30% of the positrons stopped in the chamber walls. This made it impossible to measure the absolute intensities of the long-lived component.

The pressure system consisted of a pressure cylinder, connecting pipe, and sample holder. Pressure was generated in the cylinder by a  $\frac{1}{4}$ -in. piston with "unsup-

<sup>1</sup> R. E. Bell and R. L. Graham, Phys. Rev. **90**, 644 (1953).

<sup>2</sup> P. R. Wallace, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10.

<sup>3</sup> J. Wackerle and R. Stump, Phys. Rev. **106**, 18 (1957).

<sup>4</sup> D. A. L. Paul and R. L. Graham, Phys. Rev. **106**, 16 (1957).

<sup>5</sup> M. Dresden, Phys. Rev. **93**, 1413 (1954).

<sup>6</sup> R. Stump, Bull. Am. Phys. Soc. **2**, 173 (1957).

<sup>7</sup> R. L. de Zafra and W. T. Joyner, Phys. Rev. **112**, 19 (1958).

<sup>8</sup> W. Brandt, S. Berko, and W. W. Walter, Phys. Rev. **120**, 1289 (1960).

<sup>9</sup> T. B. Daniel and R. Stump, Phys. Rev. **115**, 1599 (1959).

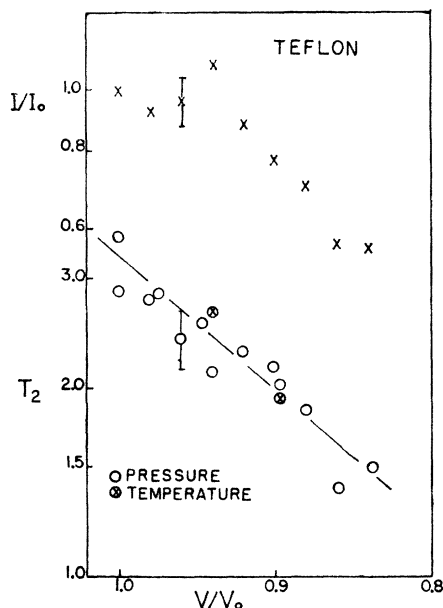


FIG. 1. Lifetime and relative intensity of orthopositronium in Teflon at reduced volume. Pressure points are those for which the volume is reduced by high pressure at 30°C; temperature points are those for which the volume is reduced by cooling to dry ice or liquid-nitrogen temperature at atmospheric pressure. Solid line from Eq. (1) and Table I. Relative intensity measurements refer only to the case in which volume is decreased by high pressure.

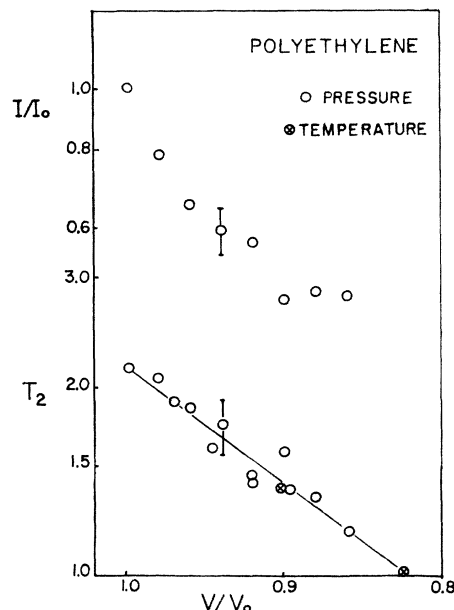


FIG. 2. Lifetime and relative intensity of orthopositronium in polyethylene at reduced volume. Pressure points are those for which the volume is reduced by high pressure at 30°C; temperature points are those for which the volume is reduced by cooling to dry ice or liquid-nitrogen temperature at atmospheric pressure. Solid line from Eq. (1) and Table I. Relative intensity measurements refer only to the case in which volume is decreased by high pressure.

ported area" packing.<sup>10</sup> The piston was driven by a 10-ton hydraulic press with hand pump. Pressure was measured by a Manganin resistance gauge<sup>11</sup> mounted in the pressure cylinder.

Temperature regulation was obtained by an iron-Constantan thermocouple on the sample holder. The thermocouple output controlled a 300-W heater. The entire assemble (sample holder, thermocouple, and heater) was in a single copper rod drilled to receive the various elements to assure uniform temperature. Around the hot rod, thermally isolated, was a water-cooled shield to protect the plastic scintillators and phototubes.

The solid samples (Lucite, Teflon, and polystyrene) were prepared by drying  $\text{Na}^{22}\text{Cl}$  solution on disks of the material. A stack of the disks, with enough material on either end to stop all of the positrons, was inserted in a steel cylinder. The piston acted directly on the sample. The change in volume was determined from the measured piston displacement; pressure was not measured.

## RESULTS

The lifetime  $\tau_2$  and intensity  $I_2$  of orthopositronium as a function of temperature and pressure have been

<sup>10</sup> P. Bridgman, *The Physics of High Pressure* (G. Bell & Sons, London, 1952).

<sup>11</sup> D. M. Warschauer and W. Paul, *Rev. Sci. Instr.* **29**, 675 (1958).

measured in a number of substances. The results are shown in Figs. 1 to 7. In each case the abscissa is the volume of the sample relative to the volume at 30°C and atmospheric pressure. The ordinate  $\tau_2$  is the mean life in millimicroseconds, and  $I/I_0$  is the ratio of the intensity  $I_2$  to the intensity  $I_0$  at 30° and one atmosphere. The absolute intensity  $I_0$  is approximately 30% but could not be determined accurately since the rather small sample holders allowed some positrons to stop in the metal walls.

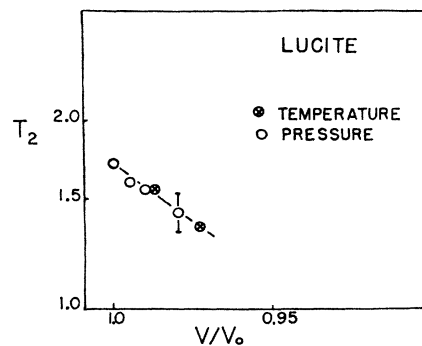


FIG. 3. Lifetime of orthopositronium in Lucite at reduced volume. Pressure points are those for which volume is reduced by high pressure at 30°C; temperature points are those for which the volume is reduced by cooling to dry ice or liquid-nitrogen temperature at atmospheric temperature. Solid line from Eq. (1) and Table I.

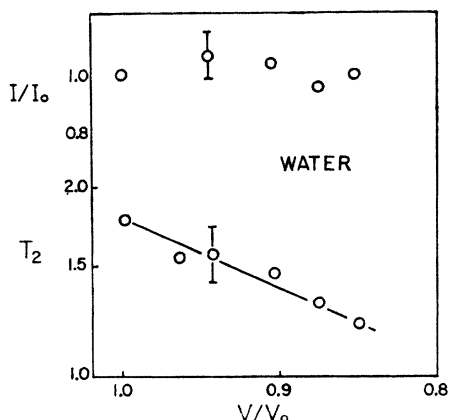


FIG. 4. Lifetime and relative intensity of orthopositronium in water as a function of volume. Volume changes are due to pressure at 30°C. Solid line from Eq. (1) and Table I.

Figures 1, 2, and 3 show the results in Teflon, polyethylene, and Lucite, respectively. Here two sets of data are presented: the mean life vs volume at room temperature and variable pressure, and mean life vs volume at atmospheric pressure and temperatures of 77 and 195°K. The volume at room temperature was obtained from the piston displacement. At low temperature the linear coefficient of thermal expansion between room temperature and the low temperature was measured. The volume coefficient, from which the relative volume was computed, was assumed to be three times the linear coefficient, i.e., the sample was assumed to be isotropic.

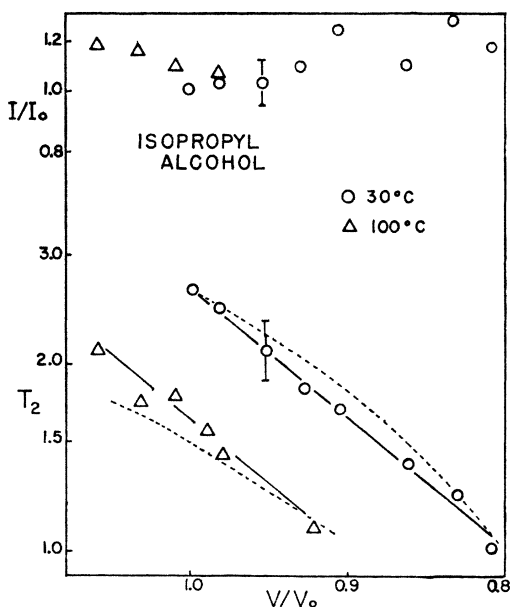


FIG. 5. Lifetime and relative intensity of orthopositronium in isopropyl alcohol as a function of volume. Volume changes are due to pressure at the indicated temperatures. Dashed lines are theoretical curves. Solid lines from Eq. (1) and Table I.

TABLE I. Lifetime of orthopositronium.  
 $\tau(T, V) = \tau_0(T) \exp(-\mu\Delta V/V)$ .

Substance	$\mu$	$\tau_0(30^\circ\text{C})$	$\tau_0(100^\circ\text{C})$	$\tau_0(200^\circ\text{C})$
		(nanosec)		
Methyl alcohol	$5.8 \pm 0.8$	$2.6 \pm 0.3$	$2.1 \pm 0.2$	
Ethyl alcohol	$5.7 \pm 0.8$	$3.0 \pm 0.4$	$2.1 \pm 0.2$	
Isopropyl alcohol	$4.9 \pm 0.6$	$2.6 \pm 0.3$	$1.6 \pm 0.2$	
Isobutyl alcohol	$5.3 \pm 0.7$	$3.4 \pm 0.3$	$2.3 \pm 0.3$	
Glycerin	$6.8 \pm 0.8$	$2.0 \pm 0.2$	$1.3 \pm 0.2$	$1.0 \pm 0.2$
Water	$2.5 \pm 0.4$	$1.8 \pm 0.2$	$1.2 \pm 0.2$	
Benzene (liquid)	$5.8 \pm 0.7$	$3.0 \pm 0.3$		
Benzene (solid)	$3.7 \pm 1.4$	$3.0 \pm 1$		
Lucite	$4.3 \pm 0.9$	$1.7 \pm 0.2$		
Teflon	$5.0 \pm 0.8$	$3.2 \pm 0.2$		
Polystyrene	$4.3 \pm 0.7$	$2.2 \pm 0.2$		

Figures 4, 5, and 6 show the results of measurements in water, isopropyl alcohol, and glycerin, respectively. In these figures are shown the mean lifetime and relative intensity at 30°C and pressures from 1 to 6000 atm. Additional isotherms are shown for isopropyl alcohol and glycerin. The relative volumes were computed from the known pressure and temperature using the *PVT* data of Bridgman.<sup>10,12</sup>

Similar measurements have been made in methyl, ethyl, and isobutyl alcohol. The results are similar to those in isopropyl alcohol, and are fit well by the empirical relationship given below [Eq. (1)] with the constant shown in Table I.

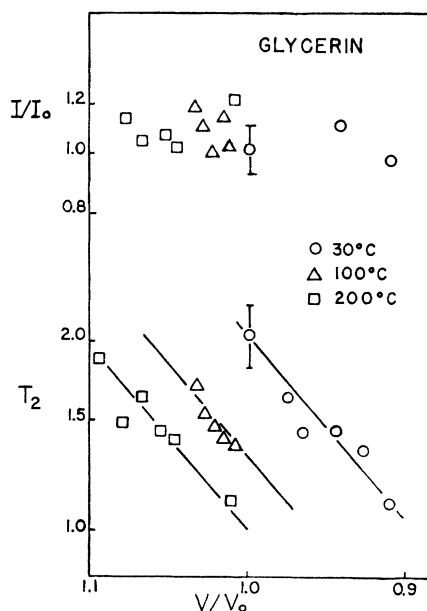


FIG. 6. Lifetime and relative intensity of orthopositronium in glycerin as a function of volume. Volume changes are due to pressure at the indicated temperatures. Solid lines from Eq. (1) and Table I.

<sup>12</sup> *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1929), Vol. 3; and *American Institute of Physics Handbook* (McGraw-Hill Book Company, New York, 1957).

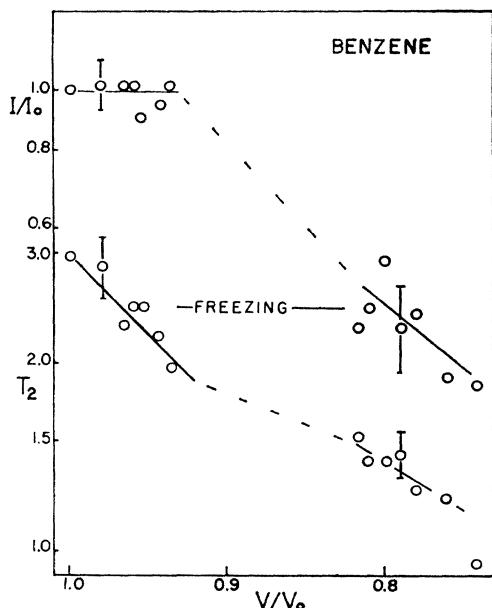


FIG. 7. Lifetime and relative intensity of orthopositronium in benzene as a function of volume. All measurements were taken at 30°C at various pressures to 5000 atm.

Figure 7 shows the results in benzene. Measurements were taken at a single temperature, 30°C, with pressures from 1 to 5000 atm. At this temperature, benzene freezes at a pressure of about 1000 atm. The conversion from pressure and temperature to relative volume was made using the data of Essex.<sup>13</sup>

The results may be summarized as follows: The intensity of the  $\tau_2$  component,  $I_2$ , is almost independent of pressure or temperature in liquids. The mean life,  $\tau_2$ , depends on the pressure and temperature  $T$  as

$$\tau_2 = \tau_0(T) \exp(\mu\Delta V/V_0). \quad (1)$$

The coefficients  $\tau_0(30^\circ\text{C})$ ,  $\tau_0(100^\circ\text{C})$ ,  $\tau_0(200^\circ\text{C})$ , and  $\mu$  are listed in Table I.  $\Delta V$  is the change in volume;  $V_0$  is the volume at 30°C. Not much significance should be attached to the exponential form of the relationship,  $\Delta V$  being so small that a linear fit would be almost as good.

#### DISCUSSION

The first and most obvious observation is that the decay of orthopositronium shows a single lifetime in any sample, i.e., there is a unique annihilation probability for all positrons in triplet positronium in a given sample. Throughout this work there was no indication of deviation from an exponential decay curve for at least the first decade drop. To account for the unique annihilation probability, it is necessary to assume that every positronium atom experiences the same average environment. As pointed out by Wallace<sup>14</sup> and Ferrell,<sup>15</sup>

the positronium atom feels a strong repulsive exchange force to other atoms. Thus, if there are local density fluctuations in a solid or a liquid, the positronium will feel a varying potential, lowest in regions of lowest density. Since the mass is so small, the positronium easily passes through potential barriers, and will diffuse through the material residing mainly in the potential wells. The unique lifetime is an indication that the annihilation probability is smaller than the probability of a diffusive jump so that the positron samples all possible environments in the material.

A calculation of the orthopositronium mean life may be made based on a crude model of the physical structure of amorphous solids and liquids. We assume that the positron lifetime is determined entirely by the size of microscopic regions of low density, which may be represented as spherical holes or vacancies in the material. In a liquid, the size and number of these holes may vary with pressure and temperature. In a solid, the number is fixed, but the size of the holes may depend on temperature and pressure. The temperature has no effect except through the changes in size or number of holes. (In fused quartz, with very low coefficient of thermal expansion, the lifetime of orthopositronium is independent of temperature.<sup>1</sup>)

We assume that the positronium atom always is found in such a hole or vacancy. In a liquid the transient nature of these holes simply requires an adiabatic movement of the positronium following the changing structure. Diffusive jumps are of course quite probable, but do not affect the problem, except that they guarantee a unique lifetime.

To estimate the lifetime, it is assumed that the positronium atom is a particle in a potential well of depth  $V_0$ . Inside the well, the probability for annihilation is simply the three-quantum rate  $\gamma_3$ ; outside the well, the probability is  $\gamma_2 + \gamma_3$ , where  $\gamma_2$  is the probability for two-quantum annihilation by pickoff and is much larger than  $\gamma_3$ . The mean lifetime is then simply

$$1/\tau = P_i\gamma_3 + P_0(\gamma_2 + \gamma_3) \sim P_0\gamma_2,$$

where  $P_i$  and  $P_0$  are the probabilities of finding the positronium inside or outside the hole, respectively.

A simple quantum-mechanical calculation for a square well leads to the approximate result:

$$\tau = \text{const} \times V^{0.87},$$

where  $V$  is the volume of the potential well and the constant is determined by the well depth and the rate  $\gamma_2$ .

The compressibility at low pressure of liquids and the plastics Teflon and polyethylene is much larger than that of crystalline solids. This excess compressibility is attributed to the squeezing out of holes in the material. If one has an estimate of the fraction of the volume of the material which is empty, then the slope of the lifetime-pressure curve may be predicted.

<sup>13</sup> H. Essex, Z. anorg. Chem. **88**, 189 (1914).

<sup>14</sup> P. R. Wallace, Phys. Rev. **100**, 738 (1955).

<sup>15</sup> R. A. Ferrell, Rev. Mod. Phys. **28**, 308 (1956).

The order of magnitude of the empty space in the plastic materials is estimated to be about 20% of the uncompressed volume. This estimate is based on the volume occupied by the material under moderately high pressure and on the high-pressure compressibility. The corresponding value of lifetime is then

$$\tau = \tau_0(1 - 5\Delta V/V)^{0.87}.$$

The slope of this, at  $\Delta V/V=0$ , leads to a value of  $\mu$ :

$$\mu = 4.35.$$

Since the basic structure of the solids is fixed, changing the temperature changes the size of the holes just as does changing the pressure. The squeezing shut of holes not only reduces the lifetime, but also reduces the probability of formation of positronium.

In liquids, since the structure is not fixed, changing the volume by temperature or pressure should not be equivalent, and some model of the structure is required. There are two sources of information on the microscopic nature of a liquid: neutron diffraction and scattering, and x-ray scattering.

In x-ray diffraction experiments<sup>16</sup> in liquids and compressed gases, it has been observed that there is structure to the diffraction pattern, showing some local ordering in the liquid state. At fixed pressure, increasing the temperature has three effects: The structure of the diffraction pattern is washed out (due to a decrease in order); the first maximum is shifted to smaller angle (due to closer spacing of ordered atoms); and the intensity of the small angle peak is increased. Neutron diffraction shows similar effects. Neutron scattering in liquids<sup>17</sup> shows that the local ordering survives for a time long compared with usual relaxation times.

These facts are not inconsistent with a theory of positron behavior in liquids based on a liquid model discussed by Frenkel.<sup>18</sup> The liquid is assumed to be

made up of a number  $z$  microcrystallites, each containing  $g$  molecules. The positronium is excluded from the microcrystallite by exchange forces, and remains in holes formed by the noncompatible grain boundaries. The vacant space in the liquids is thus divided among  $z$  holes. Positronium in one of the  $z$  empty spaces is then approximated as before by a particle in a square well. The number of regions  $z$  is a fairly rapid function of temperature. Using Frenkel's notation,

$$z \sim (1/n)[(\sigma)^3/3KT],$$

where  $n$  is the number of molecules in a unit volume,  $\sigma$  is the surface tension,  $K$  is Boltzmann's constant, and  $T$  is the temperature.

To determine the effective free space in the liquid, it is further assumed that the liquid has an equation of state of the form of Van der Waal's equation:

$$[P + P_0(T)](V - b) = F(T),$$

where  $P_0(T)$  and  $F(T)$  depend only on the temperature. The volume of a single hole is then

$$v = \left(\frac{V-b}{z}\right) = \text{const} \times \left(\frac{V-b}{T^3}\right),$$

and the lifetime is

$$\tau = \text{const} \times \left(\frac{V-b}{T^3}\right)^{0.87}.$$

The single constant is chosen to give the correct lifetime at 30°C and 1 atm. The dashed curves on Fig. 5 then show the calculated values of lifetime and the experimental values. The general trend is certainly correct. However, the model is so naive that any detailed agreement should be considered as fortuitous.

No attempt was made to fit the results of the calculation to other materials since nothing beyond qualitative agreement should be expected; and that agreement is adequately demonstrated in Fig. 5. It should be noted, however, that qualitative agreement extends not only to the liquids observed here, but also to positron measurements in liquid helium.<sup>9</sup>

<sup>16</sup> A. Eisenstein and N. S. Gingrich, Phys. Rev. **62**, 261 (1942).

<sup>17</sup> D. J. Hughes, H. Palevsky, W. Kley, and E. Tunkelo, Phys. Rev. **119**, 872 (1960).

<sup>18</sup> J. Frenkel, *Kinetic Theory of Liquids* (The Clarendon Press, Oxford, 1946).