

ENGINEERING RESEARCH INSTITUTE
THE UNIVERSITY OF MICHIGAN
ANN ARBOR

Technical Report

THE KINETIC THEORY OF A GAS IN
ALTERNATING OUTSIDE FORCE FIELDS:

A GENERALIZATION OF THE RAYLEIGH PROBLEM

C. S. Wang Chang
G. E. Uhlenbeck

Project 2457

OFFICE OF NAVAL RESEARCH, U. S. NAVY DEPARTMENT
CONTRACT NO. Nonr-1224-(15)

October 1956

TABLE OF CONTENTS

	Page
ABSTRACT	iii
OBJECTIVE	iii
I. STATEMENT OF PROBLEM	1
II. THE BROWNIAN MOTION LIMIT	3
III. THE STRONG COUPLING APPROXIMATION	4
IV. DISCUSSION OF THE APPROXIMATE RESULTS	5
V. THE EXACT SOLUTION FOR MAXWELL MOLECULES	6
VI. THE SOLUTION FOR ELASTIC SPHERES IN THE LORENTZ LIMIT IF $\omega_0 = 0$	8
VII. CONCLUDING REMARKS	12
APPENDICES	13
Appendix I. Proof of the Brownian Motion Form of the Collision Operator	14
Appendix II. Eigenvalues and Eigenfunctions of the Maxwell Collision Operator	18
Appendix III. Eigenvalues and Eigenfunctions of the Brownian Motion Form of the Collision Operator	21
Appendix IV. The Bracket Expression $[\psi_{r'l'm'}, \psi_{r\ell m}]$ in the Lorentz Limit	22

ABSTRACT

The problem of the absorption of power by a set of harmonic oscillators surrounded by a dilute gas is investigated on the basis of the linear Boltzmann equation as a function of the frequencies of the oscillator and of the outside electric field, and as a function of the type of interaction between the oscillator and the gas molecule. For the case where this interaction is an inverse fifth-power repulsion (Maxwell molecules), an exact solution of the problem is presented (Section V). Various limiting cases and approximate results are discussed.

OBJECTIVE

The main purpose was to elucidate the validity of the so-called strong collision approximation, which is often used in the kinetic theory of gases.

I. STATEMENT OF THE PROBLEM

In this report we will be concerned with the following problem. Suppose a particle of mass m is bound harmonically to a fixed point with proper frequency ω_0 ; it is surrounded by a gas of particles of mass M against which it collides according to some given force law; the gas is supposed to be in equilibrium at temperature T and the equilibrium is not affected by the motion of the particle m .¹ Finally, an outside alternating force $mE_0 \cos \omega t$ acts, say in the x -direction, on the particle m (not on the molecules of the surrounding gas). One wants to know the average power absorbed by the particle as a function of ω_0 , ω , the ratio of the masses m/M , and the type of force law between the particle and the molecules of the surrounding gas.

Clearly the problem is a generalization of the well-known problem of Rayleigh,² in which it will go over if $\omega_0 = 0$, no outside force is present, and the motion is one dimensional. The relation to the theory of the shape of absorption lines and to the theory of metals will be more or less evident and will not be further elaborated. The problem was in fact suggested in a discussion with Dr. J. M. Luttinger, because of a paradox which he encountered in the theory of metals.

In the classical form in which we stated the problem, the mathematical formulation is given by the so-called linear Boltzmann equation. Let $f(\vec{x}, \vec{v}, t) d\vec{x} d\vec{v}$ be the probability at time t that the particle m is in the space and velocity range $d\vec{x} d\vec{v}$, then f will fulfill the equation

$$\frac{\partial f}{\partial t} + v_\alpha \frac{\partial f}{\partial x_\alpha} + a_\alpha \frac{\partial f}{\partial v_\alpha} = J(f) \quad , \quad (1)$$

where \vec{a} is the acceleration produced by the forces acting on the particle m , so that

1. One may think that the gas is sufficiently dilute so that the velocity distribution of the molecules around the particle m remains the Maxwell distribution.
2. Rayleigh, Scientific Papers, Vol. 3, p. 473. See also: Ming Chen Wang, A Study of Various Solutions of the Boltzmann Equation, Dissertation, Univ. of Mich., Ann Arbor, 1942.

$$a_x = -\omega_0^2 x + E_0 \cos \omega t \quad (2)$$

$$a_y = -\omega_0^2 y ; \quad a_z = -\omega_0^2 z .$$

$J(f)$ is the collision term:

$$J(f) = \int d\vec{V} \int d\Omega g I(g, \theta) [f'F' - fF] , \quad (3)$$

where

$$F(\vec{V}) = N \left(\frac{M}{2\pi kT} \right)^{3/2} e^{-MV^2/2kT}$$

is the distribution function of the surrounding gas and the primes refer to the velocity variables; the collision $(\vec{v}, \vec{V}) \rightarrow (\vec{v}', \vec{V}')$ turns the relative velocity $g = |\vec{v} - \vec{V}|$ over the angle θ and $I(g, \theta)$ is the differential collision cross section.

The outside force $E_0 \cos \omega t$ must be considered as the perturbation which prevents the distribution function f from going to the equilibrium distribution:

$$f_0 = \left(\frac{m \omega_0}{2\pi kT} \right)^3 e^{-(mv^2 + m \omega_0^2 r^2)/2kT} . \quad (4)$$

In the steady state we now want to calculate the time average of

$$P = \bar{v}_x E_0 \cos \omega t , \quad (5)$$

where

$$\bar{v}_x(t) = \int \int d\vec{x} d\vec{v} v_x f(\vec{x}, \vec{v}, t) .$$

Clearly $f = f_0 + f_1$, where the perturbation f_1 of the distribution function will in the steady state be proportional to E_0 and vary in time like the outside force, although, of course, it will not be in phase because of the friction with the surrounding gas.

An exact solution of the problem we have found only for the case of the so-called Maxwell molecules, where one assumes that the interaction between particle m and a gas molecule is a repulsion $\sim 1/r^5$. Before turning to this special case we first will discuss some approximate solutions, assuming some approximate expressions for the collision operator which are current in the literature.

II. THE BROWNIAN MOTION LIMIT

If the particle m is very heavy compared to the gas molecule ($m/M \gg 1$), and if, in addition, we assume that the velocity \vec{v} is never very different from the equipartition value, so that v/V is always of order $(M/m)^{1/2}$, then one finds, by an expansion in powers of M/m , that the collision term $J(f)$ can be approximated by the well-known Rayleigh or Brownian motion form

$$J(f) \cong \eta \left[\frac{\partial}{\partial v_\alpha} (v_\alpha f) + \frac{kT}{m} \frac{\partial^2 f}{\partial v_\alpha \partial v_\alpha} \right], \quad (6)$$

where the friction coefficient η^3 is given by

$$\eta = \frac{16\sqrt{\pi}}{3} \frac{NM}{m} \left(\frac{M}{2kT} \right)^{5/2} \int_0^\pi d\theta \sin \theta (1 - \cos \theta) \int_0^\infty dV V^5 e^{-MV^2/2kT} I(V, \theta) .$$

Since for general $I(g, \theta)$ the proof of (6) is not easily available, we give the details in Appendix I.

With the collision term (6) it is simple to solve the problem. Multiplying the Boltzmann equation

$$\frac{\partial f}{\partial t} = -v_\alpha \frac{\partial f}{\partial x_\alpha} - a_\alpha \frac{\partial f}{\partial v_\alpha} + \eta \frac{\partial}{\partial v_\alpha} \left[v_\alpha f + \frac{kT}{m} \frac{\partial f}{\partial v_\alpha} \right] \quad (7)$$

with x_i or v_i , respectively, and integrating over the coordinate and velocity space, assuming that for large x_i and v_i f vanishes sufficiently fast, one obtains for the average values \bar{x}_i and \bar{v}_i the equations

$$\frac{d\bar{x}_i}{dt} = \bar{v}_i$$

$$\frac{d\bar{v}_i}{dt} = -\omega_0^2 \bar{x}_i + E_0 \cos \omega t \delta_{i1} - \eta \bar{v}_i, \quad (8)$$

which have an obvious physical interpretation. In the steady state

3. The assumption that v/V is always of order $(M/m)^{1/2}$ implies that on the average the particle m will feel a frictional force proportional to its velocity; the proportionality constant is η . For very large v , this will not be true anymore; the friction will then become "Newtonian," proportional to v^2 .

$$\bar{v}_i = \frac{E_0 \eta \omega^2}{(\omega^2 - \omega_0^2)^2 + \eta^2 \omega^2} \cos \omega t + \frac{E_0 \omega (\omega^2 - \omega_0^2)}{(\omega^2 - \omega_0^2)^2 + \eta^2 \omega^2} \sin \omega t ,$$

so that the average power absorbed is given by

$$\overline{P}_{B.M.} = \frac{E_0^2 \eta}{2} \frac{\omega^2}{(\omega^2 - \omega_0^2)^2 + \eta^2 \omega^2} . \quad (9)$$

For a discussion of this result, see Section IV.

III. THE STRONG COUPLING APPROXIMATION

Especially in the theory of metals, it is customary to approximate the collision term by assuming

$$J(f) \approx \frac{f_0 - f}{\tau} , \quad (10)$$

where f_0 is the equilibrium distribution (4) and τ is the relaxation time, which is a measure of the time required for the collisions to establish equilibrium. One of the main questions we will have to discuss is the question under which circumstances (10) may be used as an approximation of the collision term.

With Eq. (10), one obtains for the equation of motion of the average values \bar{x}_i, \bar{v}_i instead of (8), the equations

$$\frac{d\bar{x}_i}{dt} = \bar{v}_i - \frac{\bar{x}_i}{\tau}$$

$$\frac{d\bar{v}_i}{dt} = -\omega_0^2 \bar{x}_i + E_0 \cos \omega t \delta_{i1} - \frac{\bar{v}_i}{\tau} . \quad (11)$$

Note especially the first of these two equations. It says that the average position of the probability distribution does not change with time according to the average velocity \bar{v}_i . The origin of this paradoxical result is the fact that with (10)

$$\int d\vec{v} J(f) = \frac{1}{\tau} \int d\vec{v} (f_0 - f) ,$$

which is not necessarily zero, while from the exact expression (3) follows

$$\int d\vec{v} J(f) = 0 . \quad (12)$$

Eq. (12) is an expression of the fact that in a collision the number of particles does not change. One must say therefore that the strong collision approximation (10) violates this conservation law. A consequence of this is, as Luttinger has pointed out, that it makes a difference whether one calculates the average power absorbed with the help of the average velocity or with the help of $d\bar{x}_1/dt$. Using the average velocity, one obtains from Eq. (11) the result first derived by Van Vleck and Weisskopf:⁴

$$\overline{P}_{VW} = \frac{E_0^2 \tau}{4} \left[\frac{1}{1 + (\omega - \omega_0)^2 \tau^2} + \frac{1}{1 + (\omega + \omega_0)^2 \tau^2} \right] , \quad (13)$$

while, using $d\bar{x}/dt$, one obtains,

$$\overline{P}_L = \frac{E_0^2 \tau}{4} \frac{\omega}{\omega_0} \left[\frac{1}{1 + (\omega - \omega_0)^2 \tau^2} - \frac{1}{1 + (\omega + \omega_0)^2 \tau^2} \right] , \quad (14)$$

first given by Luttinger.⁵

IV. DISCUSSION OF THE APPROXIMATE RESULTS

If one puts in the Brownian motion result (9) $\eta = 1/\tau$, then the three results, (9), (13), and (14), can be directly compared with each other. In Figs. 1 to 5 we have plotted \overline{P} as a function of $\omega\tau$ for various values of $\omega_0\tau$. One easily verifies the following facts:

- a. For all three forms, the area under the curve is the same and equal to $\pi E_0^2/4$.
- b. For small $\omega_0\tau$, \overline{P}_{VW} will be a monotonic decreasing function of $\omega\tau$. Only for $\omega_0\tau > 1/\sqrt{3}$, \overline{P}_{VW} will have a maximum. Since both \overline{P}_L and $\overline{P}_{B.M}$ are zero for $\omega\tau = 0$, if $\omega_0\tau \neq 0$, they always will show a maximum.
- c. For $\omega_0\tau = 0$, \overline{P}_{VW} and $\overline{P}_{B.M}$ are identical.
- d. For $\omega_0\tau \gg 1$, \overline{P}_{VW} and \overline{P}_L become nearly the same, especially near the resonance peak. The $\overline{P}_{B.M}$ gives an essentially sharper resonance peak.

4. J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys., 17, 227 (1945).

5. J. M. Luttinger, Private Communication.

V. THE EXACT SOLUTION FOR MAXWELL MOLECULES

Although not quite necessary for the solution of our problem, it seems worth-while first to point out that for Maxwell molecules and for arbitrary ratio of the masses, the eigenfunctions and eigenvalues of the collision operator can be determined. For Maxwell molecules $gI(g,\theta)$ is independent of g . Putting

$$gI(g,\theta) = \sqrt{\frac{2K(M+m)}{Mm}} F(\theta) , \quad (15)$$

then $F(\theta)$ is the dimensionless function discussed in a previous report.⁶ Introducing in the exact collision term (3)

$$f = e^{-\frac{mv^2}{2kT}} h , \quad (16)$$

then from the energy conservation in the collision $(v,V) \rightarrow (v',V')$ it follows that

$$J(f) = N \sqrt{\frac{2K(M+m)}{Mm}} e^{-\frac{mv^2}{2kT}} I(h) , \quad (17)$$

where $I(h)$ is the dimensionless collision operator

$$I(h) = \frac{1}{\pi^{3/2}} \int d\vec{c} e^{-c^2} \int d\Omega F(\theta) (h' - h) \quad (18)$$

and $\vec{c} = \vec{v} (M/2kT)^{1/2}$. It is also convenient to consider h as a function of the dimensionless velocity $\vec{c} = \vec{v} (m/2kT)^{1/2}$ and then h' means $h(\vec{c}')$, where

$$\vec{c}' = \vec{c} + \frac{2M}{m+M} \vec{s} \left[\vec{s} \cdot (\sqrt{m/M} \vec{c} - \vec{c}) \right] \quad (19)$$

is the dimensionless velocity of the particle after collision.⁷

Since the operator I does not depend on the velocity \vec{c} , and since the connection between \vec{c} and \vec{c}' is linear, it is clear that the eigenfunctions of I must be polynomials in \vec{c} . Since the operator I is spherically symmetric in the velocity space \vec{c} , the dependence of the eigenfunctions on the direction

6. C. S. Wang Chang and G. E. Uhlenbeck, "On the Propagation of Sound in Monoatomic Gases," Eng. Res. Inst. Proj. M999, Univ. of Mich., Ann Arbor, October, 1952, Appendix I.

7. The symbol \vec{s} is the unit vector in the direction of closest approach; \vec{s} makes an angle $(\pi + \theta)/2$ with $\vec{g} = \vec{c} - \vec{c}'$.

of \vec{c} must be like a spherical harmonic. In fact, one can prove that the eigenfunctions are of the form

$$\psi_{r\ell m}(\vec{c}) = N_{r\ell m} c^\ell Y_{\ell m}(\theta, \phi) S_{\ell+1/2}^{(r)}(c^2), \quad (20)$$

where

$$S_{\ell+1/2}^{(r)}(c^2)$$

is the Sonine polynomial of degree r and order $\ell + 1/2$ and $N_{r\ell m}$ is a normalization factor. The $\psi_{r\ell m}$ form a complete orthogonal set of functions with the weight factor $\exp(-c^2)$. The corresponding eigenvalues are given by

$$\lambda_{r\ell} = 2\pi \int_0^\pi d\theta \sin \theta F(\theta) \left\{ \left[1 - \frac{4mM}{(m+M)^2} \sin^2 \frac{\theta}{2} \right]^{r+\ell/2} P_\ell(\cos \psi) - 1 \right\}. \quad (21)$$

P_ℓ is the Legendre polynomial, and

$$\cos \psi = \left[1 - \frac{4mM}{(m+M)^2} \sin^2 \frac{\theta}{2} \right]^{-1/2} \left(1 - \frac{2M}{m+M} \sin^2 \frac{\theta}{2} \right). \quad (21a)$$

For a proof of these statements see Appendix II. Note that the eigenfunctions (20) are independent of the mass ratio m/M , which enters only in the eigenvalues (21). The first eigenvalue $\lambda_{00} = 0$, corresponding to $\psi_{000}(\vec{c}) = \text{constant}$; this expresses the conservation of the number of particles in a collision. All other eigenvalues are negative, and this expresses the tendency of f to go to the Maxwell distribution.

The reason why our problem of the power loss can be solved exactly for Maxwell molecules lies in the fact that the velocity \vec{c} is an eigenfunction of the collision operator I , corresponding to $r = 0$, and $\ell = 1$.⁸ By developing h in the eigenfunctions $\psi_{r\ell m}$, one sees that because of the orthogonality property of the $\psi_{r\ell m}$

$$\int d\vec{c} c_i e^{-c^2} I(h) = \lambda_{01} \int d\vec{c} c_i e^{-c^2} h. \quad (22)$$

As a consequence, one obtains from the Boltzmann equation for the average values \bar{x}_i and \bar{v}_i the equations

$$\begin{aligned} \frac{d\bar{x}_i}{dt} &= \bar{v}_i \\ \frac{d\bar{v}_i}{dt} &= -\omega_0^2 x_i + E_0 \cos \omega t \delta_{i1} - \eta \bar{v}_i, \end{aligned} \quad (23)$$

8. Note that $S_k^{(0)}(x) = 1$.

where η is given by

$$\begin{aligned} \eta &= -N \sqrt{\frac{2K(M+m)}{Mm}} \cdot \lambda_{01} \\ &= 2\pi N \sqrt{\frac{2K(M+m)}{Mm}} \cdot \frac{M}{m+M} \int_0^\pi d\theta \sin \theta (1 - \cos \theta) F(\theta) . \end{aligned}$$

We see therefore that for all ratios of the masses one obtains the same functional dependence as in the Brownian motion limit. In the limit $m/M \gg 1$, the value of η goes over into the value found in the Brownian motion limit (see Appendix I). In addition, one can show as a check that the eigenfunctions of the Brownian motion form (6) of the collision operator are again the $\psi_{r\ell m}$ given by (20), while the eigenvalues are equidistant and equal to

$$\Lambda_{r\ell} = -\eta (2r + \ell) .$$

For the proof, see Appendix III.

It is therefore clear that the strong collision approximation discussed in Section III cannot have a general validity independent of the intermolecular forces. Especially, it cannot be true that in the limit $m/M \ll 1$, which is opposite to the Brownian motion limit,⁹ the collision term can be approximated by the strong coupling form (10) for all types of intermolecular force laws. Of course, it may be that the inverse fifth power law gives too "soft" collisions. It is therefore of interest to investigate other force laws and especially the case of elastic spheres.

VI. THE SOLUTION FOR ELASTIC SPHERES IN THE LORENTZ LIMIT IF $\omega_0 = 0$

If $m/M \ll 1$ and $\omega_0 = 0$, then our problem can be solved by an adaptation of the perturbation method used in the Lorentz theory of electronic conduction in metals. The distribution function f now depends only on the velocity \vec{v} and the time and fulfills the equation

$$\frac{\partial f}{\partial t} + E_0 e^{i\omega t} \frac{\partial f}{\partial v_x} = J(f) . \quad (24)$$

Considering the second term as the perturbation which prevents f from reaching the equilibrium distribution

9. It may be called the Lorentz limit, since it corresponds to the situation considered in the Lorentz theory of electronic conduction in metals.

$$f_0 = \left(\frac{m}{2\pi kT} \right)^{3/2} \exp(-mv^2/2kT) ,$$

one obtains, by putting

$$f = f_0 (1 + h) , \quad (25)$$

for h the inhomogeneous equation

$$\frac{\partial h}{\partial t} - \frac{mv_x}{kT} E_0 e^{i\omega t} = \int d\vec{V} F(V) \int d\Omega g I(g, \theta) (h' - h) . \quad (26)$$

Because of the linearity, h will be $\sim \exp(i\omega t)$ in the steady state, and in the limit $m/M \ll 1$, h will have the form

$$h = h_0(v^2) v_x e^{i\omega t} , \quad (27)$$

since in the lowest order of m/M the velocity v does not change in magnitude in a collision, and g may be replaced by v. Hence, substituting (27) in the right-hand side of (26), one gets

$$\begin{aligned} & \int d\vec{V} F(V) \int d\Omega v I(v, \theta) h_0(v^2) (v'_x - v_x) \\ &= -2\pi N h_0(v^2) v_x \int_0^\pi d\theta \sin \theta (1 - \cos \theta) v I(v, \theta) . \end{aligned}$$

Therefore, for elastic spheres [$I(v, \theta) = 1/4 \sigma^2$, where σ is the average of the diameters of the spheres with masses m and M] one obtains

$$h_0(v^2) = \frac{m E_0}{kT} \frac{1}{i\omega + \pi \sigma^2 N v} . \quad (28)$$

Introducing the relaxation time

$$\tau = \frac{1}{\pi \sigma^2 N} \sqrt{\frac{m}{2kT}} , \quad (29)$$

one gets for the average velocity in the x-direction

$$\bar{v}_x = \frac{8 E_0 \tau}{3 \sqrt{\pi}} e^{i\omega t} \int_0^\infty dc c^4 e^{-c^2} \frac{1}{c + i\omega \tau} , \quad (30)$$

and hence for the average power absorbed

$$\begin{aligned} \overline{P} &= \frac{4 E_0^2 \tau}{3 \sqrt{\pi}} \int_0^\infty dc c^5 e^{-c^2} \frac{1}{c^2 + \omega^2 \tau^2} \\ &= \frac{2 E_0^2 \tau}{3 \sqrt{\pi}} [1 - \omega^2 \tau^2 + \omega^4 \tau^4 e^{+\omega^2 \tau^2} \text{Ei}(-\omega^2 \tau^2)] \end{aligned} \quad (31)$$

where $\text{Ei}(y)$ is the exponential integral

$$\text{Ei}(-y) = \int_y^\infty dx \frac{e^{-x}}{x} .$$

\overline{P} as function of ω is shown in Fig. 1. One easily verifies that the area under the curve is again $\pi E_0^2/4$, just as for all the other curves. One sees that the elastic-sphere result lies between the Van Vleck-Weisskopf and the Luttinger results. In fact, for large $\omega\tau$

$$\overline{P}_{\text{VW}} \sim \frac{2}{\omega^2 \tau^2} \quad \overline{P}_{\text{L}} \sim \frac{4}{\omega^2 \tau^2} ,$$

while from (31) one obtains

$$\overline{P} \sim \frac{16}{3 \sqrt{\pi} \omega^2 \tau^2} = \frac{3.01}{\omega^2 \tau^2} .$$

One can solve the problem also in another way, which is of interest since it may be generalizable to the case where ω_0 is not zero. Expand the perturbation h in the eigenfunctions (20) of the collision operator for Maxwell molecules. Then we can write

$$f = f_0 \left[1 + \sum_{r,l} \alpha_{rl} \psi_{rl}(\vec{c}) e^{i\omega t} \right] , \quad (32)$$

where $c = v (m/2kT)^{1/2}$ and α_{rl} are the development coefficients.¹⁰ Substituting in the Boltzmann equation (24), multiplying by $\psi_{r'l'} \exp(-c^2)$, and integrating over \vec{c} , one obtains a set of linear equations in α_{rl} .¹¹

10. Because of the axial symmetry of the problem we can take $m = 0$.

11. The N_{rl} are normalization constants, determined by

$$\int d\vec{c} \exp(-c^2) \psi_{rl}^2 = 1 ,$$

which gives

$$N_{rl} = \sqrt{\frac{r! (l + 1/2)}{\pi (l + 1/2 + r)!}} .$$

$$i \omega \alpha_{rl} - \sqrt{\frac{m}{2kT}} \frac{2 E_0}{N_{01}} \delta_{r0} \delta_{l1} = \sum_{r', l'} [\psi_{rl}, \psi_{r'l'}] \alpha_{r'l'} , \quad (33)$$

where the bracket symbols are defined by:

$$[\psi_{rl}, \psi_{r'l'}] = \int d\vec{c} e^{-c^2} \psi_{rl}(\vec{c}) \int d\vec{V} F(V) \cdot \\ \cdot \int d\Omega g I(g, \theta) [\psi_{r'l'}(\vec{c}') - \psi_{r'l'}(\vec{c})] .$$

For arbitrary ratio of m/M the calculation of the bracket symbols is complicated, but in the Lorentz limit $m/M \ll 1$ the result is again simple. As shown in Appendix 4 one obtains in this limit for elastic spheres:

$$[\psi_{r'l'}, \psi_{rl}] = - \frac{1}{2\tau} \frac{N_{rl} N_{r'l'}}{2l+1} \delta_{ll'} \sum_s \frac{(s+l+1)! (r'-3/2-s)! (r-3/2-s)!}{s! (r'-s)! (r-s)!} . \quad (34)$$

Since the equations (33) are not coupled through the index l , and since the inhomogeneous part contains only $l = 1$, we can restrict ourselves throughout to $l = 1$. The equations (33) can then be written in the form

$$i \omega \alpha_r - \frac{1}{\tau} \sum_{r'=0}^{\infty} b_{rr'} \alpha_{r'} = \sqrt{\frac{m}{2kT}} \frac{2 E_0}{N_{01}} \delta_{r0} , \quad (35)$$

with $r = 0, 1, 2 \dots$ and where $b_{rr'}$ is the bracket symbol $\tau[\psi_{r1}, \psi_{r'1}]$. The average velocity in the x-direction depends on α_0 ; in fact,

$$\bar{v}_x = \frac{N_{01} \alpha_0}{2} \sqrt{\frac{2kT}{m}} e^{i\omega t} .$$

From (35) follows

$$\alpha_0 = \sqrt{\frac{m}{2kT}} \frac{2 E_0}{N_{01}} \tau \frac{D_{00}(i\omega\tau)}{D(i\omega\tau)} ,$$

where D is the determinant $\| i\omega\tau \delta_{rr'} - b_{rr'} \|$ and D_{00} is the minor of the (0,0) element. Thus

$$\bar{v}_x = E_0 \tau \frac{D_{00}(i\omega\tau)}{D(i\omega\tau)} e^{i\omega t} , \quad (36)$$

which must be compared with Eq. (30). The identity of (30) and (36) for $\omega = 0$

has been shown by Chapman.¹² We also verified the identity for large ω . A complete formal proof of the identity is lacking.

VII. CONCLUDING REMARKS

If ω_0 is not zero, then the perturbation h will depend on the coordinates as well as on \vec{v} and t . It seems feasible to generalize the second method of the previous section by developing h into products $\psi_{r\ell m}(\vec{x}) \psi_{r\ell m}(\vec{v})$, using the same type of functions in both \vec{x} and \vec{v} , and again considering the Lorentz limit. However, the details have not yet been worked out.

Presumably for elastic spheres and in the Lorentz limit, the result for $\omega_0 \neq 0$ will always lie between the Van Vleck-Weisskopf and the Luttinger result. There is one feature which the exact result will have in common with the Luttinger result, namely, that for $\omega_0 \neq 0$ and $\omega = 0$, \overline{P} will be zero. This is clear, because in this case the constant outside force will only polarize the oscillator and in the steady state f will be the Maxwell-Boltzmann distribution

$$f \sim \exp \left(- \frac{m}{2kT} \left\{ v^2 + \omega_0^2 \left[\left(x + \frac{E_0}{\omega_0^2} \right)^2 + y^2 + z^2 \right] \right\} \right),$$

so that \overline{v}_x is zero.

12. S. Chapman, J. London Math. Soc., 8, 266 (1933).

APPENDICES

APPENDIX I

PROOF OF THE BROWNIAN MOTION FORM
OF THE COLLISION OPERATOR

As in Section V we put in the exact collision term (3)

$$f = e^{-\frac{mv^2}{2kT}} h, \quad (1-A)$$

then again it follows that

$$J(f) = N \left(\frac{M}{2\pi kT} \right)^{3/2} e^{-\frac{mv^2}{2kT}} I(h), \quad (2-A)$$

where

$$I(h) = \int d\vec{V} e^{-\frac{MV^2}{2kT}} \iint d\epsilon d\theta \sin \theta g I(g, \theta) (h' - h). \quad (3-A)$$

Since for $m/M \gg 1$, \vec{v}' differs very little from v , one may make a Taylor expansion:

$$h' - h = (v'_\alpha - v_\alpha) \frac{\partial h}{\partial v_\alpha} + \frac{1}{2} (v'_\alpha - v_\alpha)(v'_\beta - v_\beta) \frac{\partial^2 h}{\partial v_\alpha \partial v_\beta} + \dots \quad (4-A)$$

From the momentum conservation follows

$$\vec{v}' - \vec{v} = -\frac{M}{m+M} (\vec{g}' - \vec{g}), \quad (5-A)$$

where $\vec{g} = \vec{V} - \vec{v}$, $\vec{g}' = \vec{V}' - \vec{v}'$, are the relative velocities before and after collision.¹³ Introducing (4-A) and (5-A) one can integrate over the azimuthal angle ϵ , since only $\vec{g}' - \vec{g}$ depends on ϵ . Next, introduce in the velocity space \vec{V} polar coordinates with the direction of \vec{v} as polar axis. One then can again integrate over the azimuthal angle of \vec{V} . In these two integrations over azimuthal angles, the following general formulas are used, which are easily verified:

¹³. Of course, $|\vec{g}'| = |\vec{g}|$, and θ is the angle between \vec{g}' and \vec{g} .

$$\int_0^{2\pi} d\phi (A_i - B_i) = 2\pi \left(\frac{A}{B} \cos \Theta - 1 \right) B_i$$

$$\int_0^{2\pi} d\phi (A_i - B_i) (A_j - B_j) = 2\pi \left\{ B_i B_j \left[\left(\frac{A}{B} \cos \Theta - 1 \right)^2 - \frac{1}{2} \frac{A^2}{B^2} \sin^2 \Theta \right] + \frac{1}{2} A^2 \sin^2 \Theta \delta_{ij} \right\}.$$

In here \vec{B} is a fixed vector and Θ, ϕ are the polar angles of the vector \vec{A} with respect to \vec{B} .

Now it is convenient to use dimensionless variables:

$$\vec{c} = \sqrt{\frac{m}{2kT}} \vec{v} \quad \vec{C} = \sqrt{\frac{M}{2kT}} \vec{V}. \quad (6-A)$$

Note that we use different units for \vec{v} and \vec{V} . Assuming, as we will from now on, that c and C are of the same order of magnitude means that we have introduced our second assumption, namely, that \vec{v} never differs very much from the equipartition value. With these units

$$g = \sqrt{\frac{2kT}{M}} C \left(1 - 2\sqrt{\frac{M}{m}} \frac{c}{C} \cos \phi + \frac{M}{m} \frac{c^2}{C^2} \right)^{1/2},$$

where ϕ is the angle between \vec{C} and \vec{c} . Up to order $(M/m)^{1/2}$, one has therefore

$$gI(g, \theta) = \sqrt{\frac{2kT}{M}} CI \left(\sqrt{\frac{2kT}{M}} C, \theta \right) \left[1 - \sqrt{\frac{M}{m}} \frac{c}{C} \cos \phi \left(1 + \frac{C}{I} \frac{\partial I}{\partial C} \right) \right].$$

Developing also the rest of the integrand in powers of M/m , one obtains

$$I(h) = 4\pi^2 \frac{M}{m} \left(\frac{2kT}{M} \right)^2 \int_0^\pi d\theta \sin \theta (1 - \cos \theta) \int_0^\infty dC C^3 e^{-C^2} \cdot$$

$$\cdot \int_0^\pi d\phi \sin \phi I \left(\sqrt{\frac{2kT}{M}} C, \theta \right) \left[1 - \sqrt{\frac{M}{m}} \frac{c}{C} \cos \phi \left(1 + \frac{C}{I} \frac{\partial I}{\partial C} \right) \right].$$

$$\cdot \left\{ \sqrt{\frac{m}{M}} \cos \phi \frac{C}{c} c_\alpha \frac{\partial h}{\partial c_\alpha} - \left[c_\alpha \frac{\partial h}{\partial c_\alpha} + \frac{1}{8} (3 \cos \theta - 1) (3 \cos^2 \phi - 1) \right] \cdot \right.$$

$$\cdot \left. \frac{C^2}{c^2} c_\alpha c_\beta \frac{\partial^2 h}{\partial c_\alpha \partial c_\beta} + \frac{1}{8} \left(\cos^2 \phi - 3 - \cos \theta (3 \cos \phi - 1) \right) C^2 \frac{\partial^2 h}{\partial c_\alpha \partial c_\alpha} \right]$$

$$+ O\left(\sqrt{\frac{M}{m}}\right) \}.$$

Carrying out the ϕ integration, keeping under the integral sign only the terms of order one,¹⁴ and making the partial integration

$$\int_0^\infty dC C^4 e^{-C^2} \frac{\partial I}{\partial C} = - \int_0^\infty dC e^{-C^2} I \cdot (4C^3 - 2C^5) ,$$

one obtains

$$I(h) = \frac{8\pi^2}{3} \frac{M}{m} \left(\frac{2kT}{M}\right)^2 \int_0^\pi d\theta \sin \theta (1 - \cos \theta) \int_0^\infty dC e^{-C^2} \cdot C^5 I\left(\sqrt{\frac{2kT}{M}} C, \theta\right) \left(\frac{\partial^2 h}{\partial c_\alpha \partial c_\alpha} - 2c_\alpha \frac{\partial h}{\partial c_\alpha}\right) .$$

Introducing this expression in (2-A), and going back to the original velocity variables \vec{v} and \vec{V} , and to the original distribution function f , one gets

$$J(f) = \eta \frac{\partial}{\partial v_\alpha} \left(v_\alpha f + \frac{kT}{m} \frac{\partial f}{\partial v_\alpha} \right) ,$$

with

$$\eta = \frac{16\sqrt{\pi}}{3} N \frac{M}{m} \left(\frac{M}{2kT}\right)^{5/2} \int_0^\pi d\theta \sin \theta (1 - \cos \theta) \int_0^\infty dV V^5 e^{-\frac{MV^2}{2kT}} I(V, \theta) .$$

For a repulsive force Kr^{-s} , we write for the differential cross section¹⁵

$$I(g, \theta) = g^{-\frac{4}{s-1}} F(\theta, K, s) ,$$

and then

$$\eta = \frac{8\sqrt{\pi}}{3} \frac{NM}{m} \left(\frac{2kT}{M}\right)^{\frac{s-5}{2(s-1)}} \Gamma\left(\frac{3s-5}{s-1}\right) \int_0^\pi d\theta \sin \theta (1 - \cos \theta) F(\theta, K, s) .$$

Especially for Maxwell molecules ($s = 5$),¹⁶

14. It needs some further argument to show that it would be inconsistent to include higher-order terms in M/m , since then also the further terms in the Taylor development (4-A) would have to be included.

15. C. S. Wang Chang and G. E. Uhlenbeck, "Transport Phenomena in Very Dilute Gases," CM 579, UMH-3-F, Univ. of Mich.

16. $F(\theta) = \sqrt{\frac{mM}{2K(m+M)}} F(\theta, K, 5) \cong \sqrt{\frac{M}{2K}} F(\theta, K, 5)$ is the dimensionless collision cross section used in Section V.

$$\eta = 2\pi N \frac{M}{m} \sqrt{\frac{2kT}{M}} \int_0^\pi d\theta \sin \theta (1 - \cos \theta) F(\theta) ,$$

and for elastic spheres ($s = \infty$; $\sigma = \text{diameter}$),¹⁷

$$\eta = \frac{8\sqrt{\pi}}{3} \frac{NM\sigma^2}{m} \sqrt{\frac{2kT}{M}} .$$

17. For elastic spheres the Brownian motion form of the collision operator was first derived by M. S. Green, J. Chem. Phys., 19, 1036 (1951).

APPENDIX II

EIGENVALUES AND EIGENFUNCTIONS OF THE MAXWELL COLLISION OPERATOR

The dimensionless collision operator¹⁸

$$I(h) = \frac{1}{\pi^{3/2}} \int d\vec{c} e^{-c^2} \int d\Omega F(\theta) [h(\vec{c}') - h(\vec{c})]$$

can be written in the standard form¹⁸

$$I(h) = -A_0 h + \frac{1}{\pi^{3/2}} \left(\frac{M}{m}\right)^{3/2} e^{c^2} \int d\vec{c}' K(\vec{c}, \vec{c}') h(\vec{c}'),$$

where

$$A_0 = 2\pi \int_0^\pi d\theta \sin \theta F(\theta)$$

$$K(\vec{c}, \vec{c}') = 4\pi \left(\frac{m+M}{M}\right)^3 \exp \left\{ -\frac{m+M}{2m} \left[c^2 + c'^2 + \frac{m-M}{2M} (\vec{c} - \vec{c}')^2 \right] \right\}.$$

$$\cdot \int_0^\pi d\theta \cos \frac{\theta}{2} \csc^2 \frac{\theta}{2} F(\theta) \exp \left[-\frac{(m+M)^2}{4mM} (\vec{c} - \vec{c}')^2 \cot^2 \frac{\theta}{2} \right].$$

$$\cdot J_0 \left(-i \frac{m+M}{m} c c' \sin(\vec{c}, \vec{c}') \cot \frac{\theta}{2} \right).$$

We now will verify that

$$\psi_{r\ell m} = c^\ell S_{\ell + \frac{1}{2}}^{(r)}(c^2) Y_{\ell m}(\phi, \chi)$$

is an eigenfunction of I. Let ϕ', χ' be the polar angles of \vec{c}' with respect to the same set of axes as used for \vec{c} . For the integration over \vec{c}' we take the direction of \vec{c} as polar axis and let ϕ_1, χ_1 then be the polar angles.

18. D. Enskog, "Kinetische Theorie der Vorgänge in mässig verdünnten Gasen," Dissertation, Uppsala, 1917, p. 154. Note that A_0 is divergent and really should be kept together with the second term.

The integration over χ_1 can be performed, using

$$\int_0^{2\pi} d\chi_1 Y_{lm}(\phi', \chi') = 2\pi P_l(\cos \phi_1) Y_{lm}(\phi, \chi), \quad (7-A)$$

and one obtains

$$\begin{aligned} I(\psi_{rlm}) &= -A_0 \psi_{rlm} + \sqrt{\pi} \left(\frac{M+m}{\sqrt{mM}} \right)^3 e^{-\frac{(m-M)^2}{4mM} c^2} \\ &\cdot Y_{lm}(\phi, \chi) \int_0^\pi d\theta \cos \frac{\theta}{2} \csc^2 \frac{\theta}{2} F(\theta) e^{-\frac{(M+m)^2}{4mM} c^2 \cot^2 \frac{\theta}{2}} \\ &\cdot \int_0^\pi dc' c'^{\ell+2} S_{\ell+\frac{1}{2}}^{(r)}(c', z) e^{-\frac{(m+M)^2}{4mM} c'^2 \csc^2 \frac{\theta}{2}} \\ &\cdot \int_0^\pi d\phi_1 \sin \phi_1 P_\ell(\cos \phi_1) J_0 \left(-i \frac{m+M}{m} cc' \sin \phi_1 \cot \frac{\theta}{2} \right) \\ &\cdot \exp \left\{ 2cc' \left[\frac{m^2 - M^2}{4mM} + \frac{(m+M)^2}{4mM} \cot^2 \frac{\theta}{2} \right] \cos \phi_1 \right\}. \end{aligned}$$

Putting

$$\begin{aligned} z &= -i \frac{(m+M)^2}{2mM} \csc^2 \frac{\theta}{2} \sqrt{1 - \frac{4mM}{(m+M)^2} \sin^2 \frac{\theta}{2}} cc' \equiv \alpha c' \\ \cos \psi &= \frac{1 - \frac{2M}{m+M} \sin^2 \frac{\theta}{2}}{\sqrt{1 - \frac{4mM}{(m+M)^2} \sin^2 \frac{\theta}{2}}}, \end{aligned}$$

then the last integral can be carried out, using

$$\begin{aligned} \int_0^\pi d\phi_1 \sin \phi_1 P_\ell(\cos \phi_1) e^{iz \cos \phi_1 \cos \psi} J_0(z \sin \phi_1 \sin \psi) &= \\ &= \sqrt{\frac{2\pi}{z}} i^\ell P_\ell(\cos \psi) J_{\ell+\frac{1}{2}}(z). \end{aligned}$$

Writing $z = \alpha c'$, the integral over c' can be carried out next with the help of the formula

$$\int_0^\infty dc' c'^{l+\frac{3}{2}} S_{l+\frac{1}{2}}^{(r)}(c'^2) e^{-q^2 c'^2} J_{l+\frac{1}{2}}(\alpha c') =$$

$$= \frac{\alpha^{l+\frac{1}{2}}}{(2q^2)^{l+\frac{3}{2}}} \left(\frac{q^2-1}{q}\right)^r e^{-\frac{\alpha^2}{4q^2}} S_{l+\frac{1}{2}}^{(r)} \left[-\frac{\alpha^2}{4q^2(q^2-1)} \right],$$

where q^2 is an abbreviation for

$$q^2 = \frac{(m+M)^2}{4mM} \csc^2 \frac{\theta}{2}.$$

Putting everything together, one obtains

$$I(\psi_{rlm}) = -A_0 \psi_{rlm} + 2\pi \psi_{rlm} \cdot$$

$$\int_0^\pi d\theta \sin \theta F(\theta) P_l(\cos \psi) \left[1 - \frac{4mM}{(m+M)^2} \sin^2 \frac{\theta}{2} \right]^{r+\frac{l}{2}},$$

which is $\lambda_{rl} \psi_{rlm}$, where the eigenvalue λ_{rl} is given by the equations (21), (21a).

APPENDIX III

EIGENVALUES AND EIGENFUNCTIONS OF THE BROWNIAN
MOTION FORM OF THE COLLISION OPERATOR

The question is to find the eigenfunctions and eigenvalues of the differential equation

$$\frac{\partial}{\partial v_{\alpha}} \left(v_{\alpha} f + \frac{kT}{m} \frac{\partial f}{\partial v_{\alpha}} \right) = \frac{\Lambda}{\eta} f .$$

Introducing the dimensionless velocity $\vec{c} = \vec{v} (m/2kT)^{1/2}$, we find

$$\Delta f + c_{\alpha} \frac{\partial f}{\partial c_{\alpha}} + 6f = \frac{2\Lambda}{\eta} f .$$

The angular dependence is clearly like a spherical harmonic, and putting

$$f = c^{\ell} R(c) e^{-c^2} Y_{\ell m}(\theta, \phi) ,$$

one gets for the radial function R,

$$\frac{d^2 R}{dc^2} + \left[\frac{2(\ell+1)}{c} - 2c \right] \frac{dR}{dc} - \left[2\ell + \frac{2\Lambda}{\eta} \right] R = 0 ,$$

or using $x = c^2$ as independent variable,

$$x \frac{d^2 R}{dx^2} + \left(\ell + \frac{3}{2} - x \right) \frac{dR}{dx} - \left(\frac{\ell}{2} + \frac{2\Lambda}{\eta} \right) R = 0 .$$

Comparing this equation with the equation for the Sonine polynomial $S_t^{(r)}(x)$,

$$x \frac{d^2 S_t^{(r)}}{dx^2} + (t+1-x) \frac{dS_t^{(r)}}{dx} + r S_t^{(r)} = 0 ,$$

one sees that $R = S_{\ell + \frac{1}{2}}^{(r)}(c^2)$ and that $r = - \left(\frac{\ell}{2} + \frac{2\Lambda}{\eta} \right)$, so that the eigenvalue

$$\Lambda_{\ell r} = - \eta(2r + \ell) .$$

It is also easy to verify that the exact formula (21) in Section V leads in the Brownian motion limit to the same result.

APPENDIX IV

 THE BRACKET EXPRESSION $[\psi_{r'l'm'}, \psi_{r\ell m}]$ IN THE LORENTZ LIMIT

In the limit $m/M \ll 1$ we will calculate the bracket expression for a repulsive intermolecular force equal to Kr^{-s} , since this contains the Maxwell model and the elastic-sphere model as limiting cases. Writing as in Appendix I,

$$gI(g, \theta) = g^{\frac{s-5}{s-1}} F(\theta, K, s),$$

the bracket expression becomes

$$\begin{aligned} [\psi_{r'l'm'}, \psi_{r\ell m}] &= N \left(\frac{m}{2kT} \right)^{3/2} \left(\frac{M}{2\pi kT} \right)^{3/2} \int d\vec{v} e^{-\frac{mv^2}{2kT}} \\ &\cdot \int d\vec{V} e^{-\frac{MV^2}{2kT}} \int_0^\pi \int_0^{2\pi} d\epsilon d\theta \sin \theta g^{\frac{s-5}{s-1}} F(\theta, K, s) \\ &\cdot \psi_{r'l'm'} \left(\vec{v} \sqrt{\frac{m}{2kT}} \right) \left[\psi_{r\ell m} \left(\vec{v} \sqrt{\frac{m}{2kT}} \right) - \psi \left(\vec{v} \sqrt{\frac{m}{2kT}} \right) \right]. \end{aligned}$$

Since mv^2 is of the same order of magnitude as MV^2 , in the limit $m/M \ll 1$ and to the lowest order in m/M , one can replace \vec{g}' by $-\vec{v}'$ and \vec{g} by $-\vec{v}$. Using Eq. (7-A) of Appendix II, the integral over ϵ can be carried out, and also the integral over \vec{V} is immediate. With dimensionless velocity variables, one then obtains

$$\begin{aligned} [\psi_{r'l'm'}, \psi_{r\ell m}] &= 2\pi N \left(\frac{2kT}{m} \right)^{2(s-1)} \int_0^\pi d\theta \sin \theta F(\theta, K, s) \\ &\cdot [P_\ell(\cos \theta) - 1] \int d\vec{c} e^{-c^2} c^{\frac{s-5}{s-1}} \psi_{r'l'm'}(\vec{c}) \psi_{r\ell m}(\vec{c}). \end{aligned}$$

Since the angular dependence of the $\psi_{r\ell m}$ is a spherical harmonic, the integral over the directions of \vec{c} is immediate. Putting in the explicit expression for the Sonine polynomials, the integral over c can be carried out in each term and the result is a double sum, of which one sum can be evaluated with the help of the formula

$$\sum_s \binom{m}{k-s} \binom{n+s}{n} (-1)^s = \binom{m-n-1}{k}.$$

One obtains

$$[\Psi_{r'l'm'}, \Psi_{rlm}] = \frac{4\pi^2}{2l+1} N_{rl} N_{r'l'} \delta_{ll'} \delta_{mm'} \left(\frac{2kT}{m}\right)^{\frac{s-5}{2(s-1)}} \cdot$$

$$\cdot \int_0^\pi d\theta \sin \theta F(\theta, K, s) [P_l(\cos \theta) - 1] \frac{1}{\left\{[-1 - \frac{s-5}{2(s-1)}]!\right\}^2} \cdot$$

$$\cdot \sum_p \frac{\left[p + \frac{l+l'}{2} + \frac{1}{2} + \frac{s-5}{2(s-1)}\right]! \left[r - p - 1 - \frac{s-5}{2(s-1)}\right]! \left[r' - p - 1 - \frac{s-5}{2(s-1)}\right]!}{p!(r'-p)!(r-p)!}$$

Since $\frac{1}{2} \geq \frac{s-5}{2(s-1)} \geq 0$ for $\infty \geq s \geq 5$, only the case of Maxwell molecules ($s = 5$) needs special consideration since then factorials of negative integers appear. In this case one finds either directly or by a limit consideration,

$$[\Psi_{r'l'm'}, \Psi_{rlm}] = \frac{4\pi^2 N}{2l+1} N_{rl} N_{r'l'} \delta_{rr'} \delta_{ll'} \delta_{mm'} \cdot$$

$$\cdot \frac{\left(r+l+\frac{1}{2}\right)!}{r!} \int_0^\pi d\theta \sin \theta F(\theta, K, 5) [P_l(\cos \theta) - 1] \cdot$$

Finally, for elastic spheres ($s = \infty$), one gets

$$[\Psi_{r'l'm'}, \Psi_{rlm}] = \frac{8\pi\sigma^2 N}{2l+1} N_{rl} N_{r'l'} \delta_{ll'} \delta_{mm'} \sqrt{\frac{2kT}{m}} \cdot$$

$$\cdot \sum_p \frac{(p+l+1)! \left(r - \frac{3}{2} - p\right)! \left(r' - \frac{3}{2} - p\right)!}{p!(r'-p)!(r-p)!}$$

which reduces to the expression (34) used in Section VI.

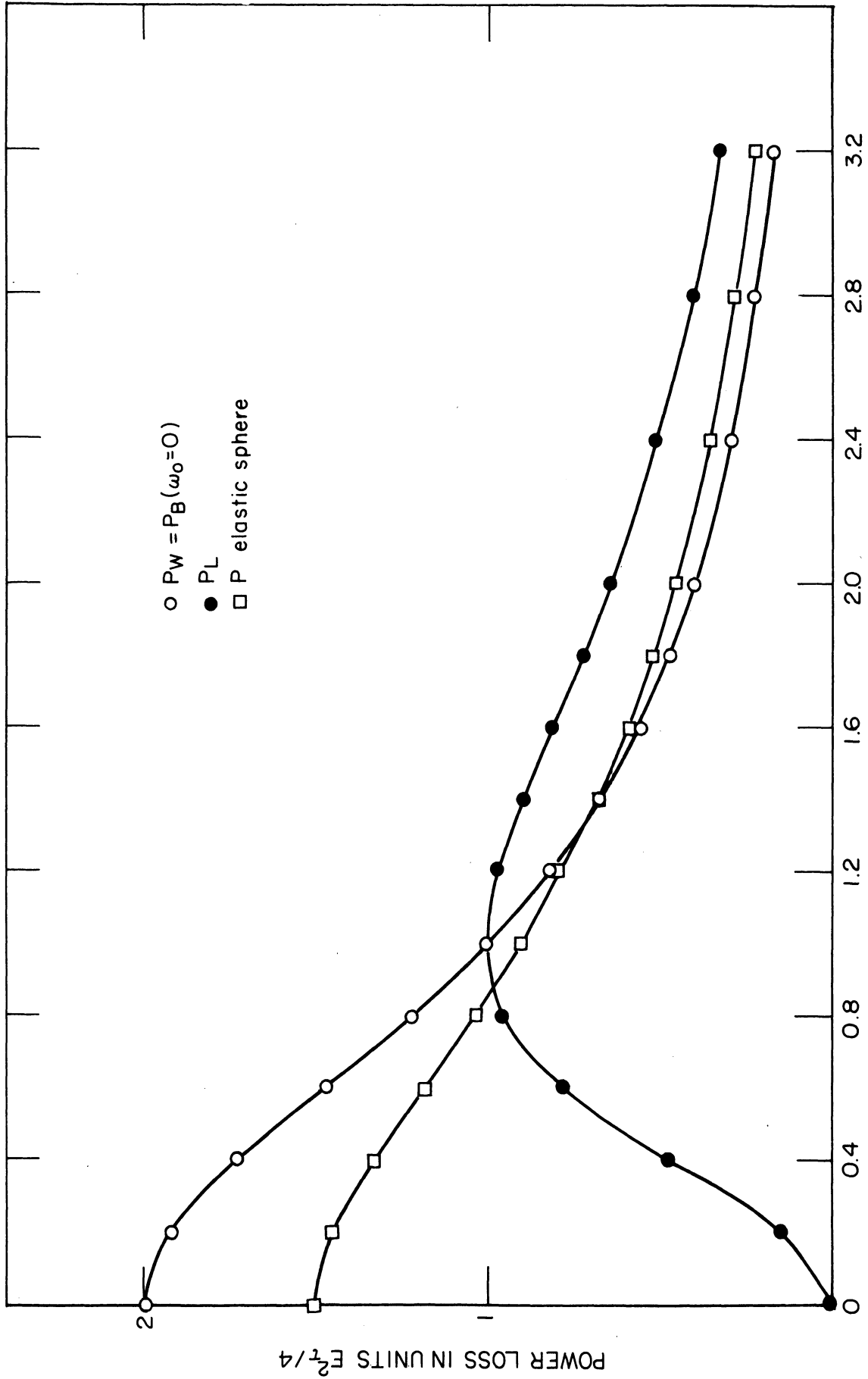


Fig. 1. $\omega_0 \tau = 0$.

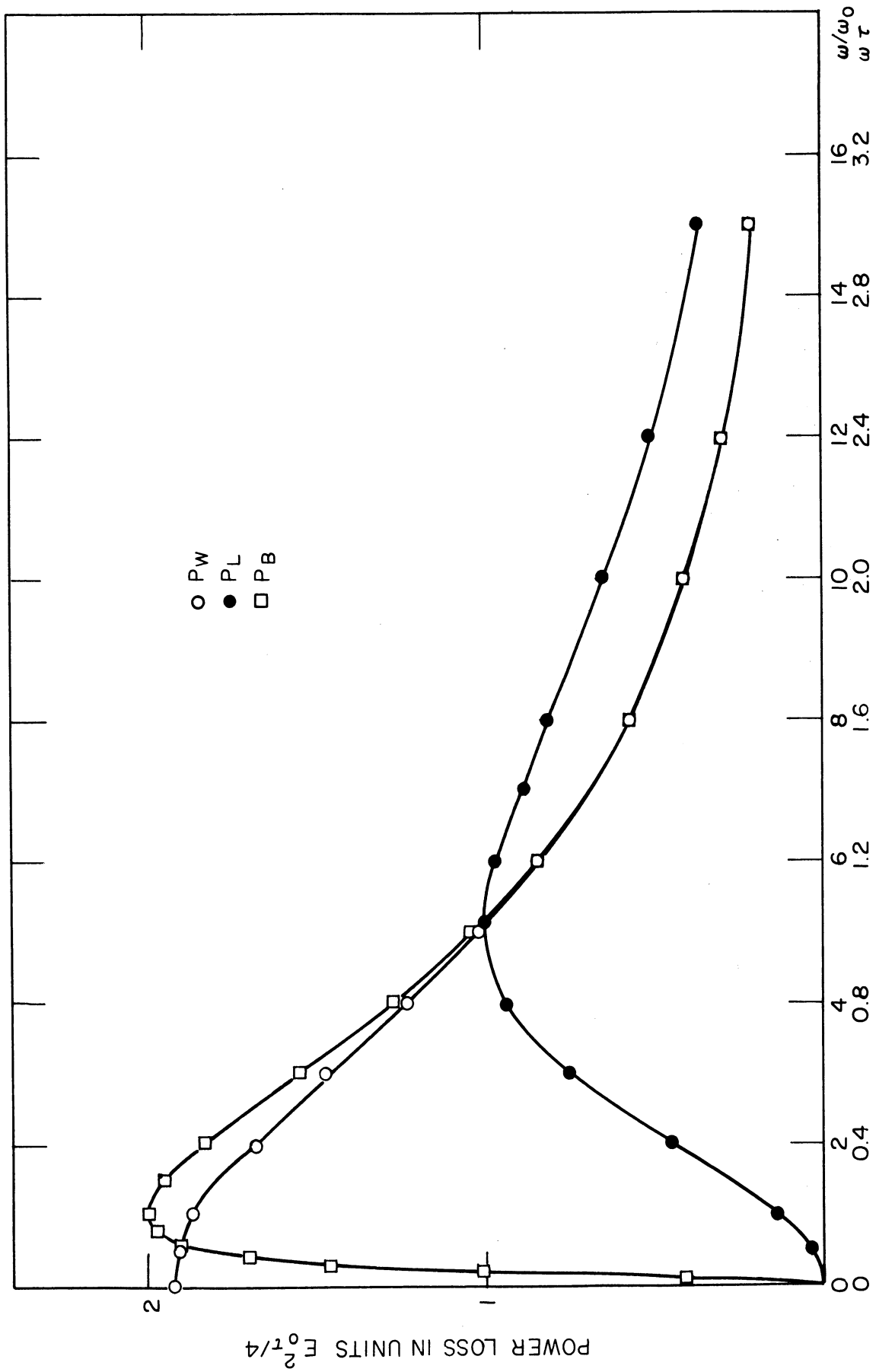


Fig. 2. $\omega_0 \tau = 0.2$.

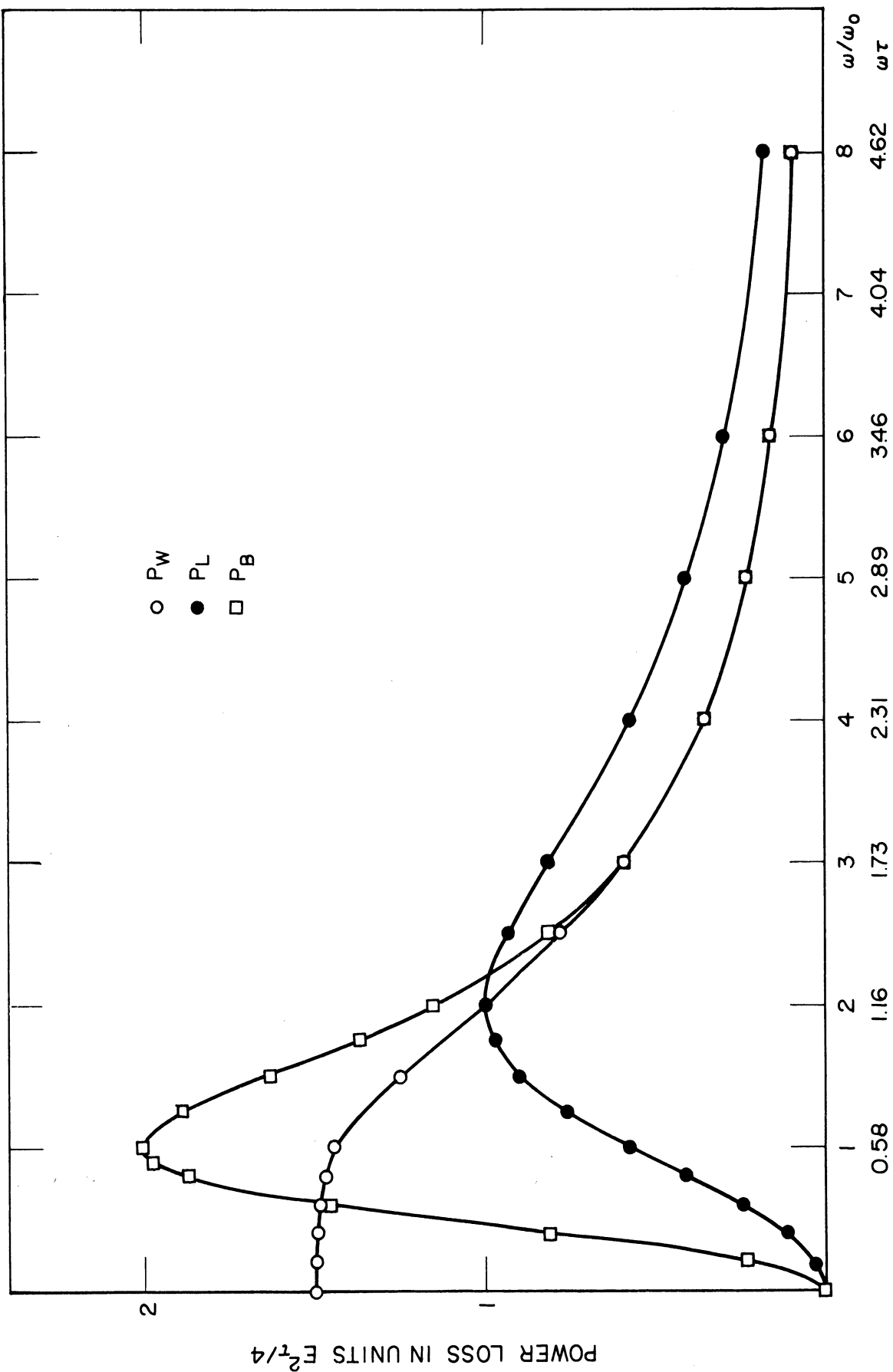


Fig. 3. $\omega_0\tau = 1/\sqrt{3}$.

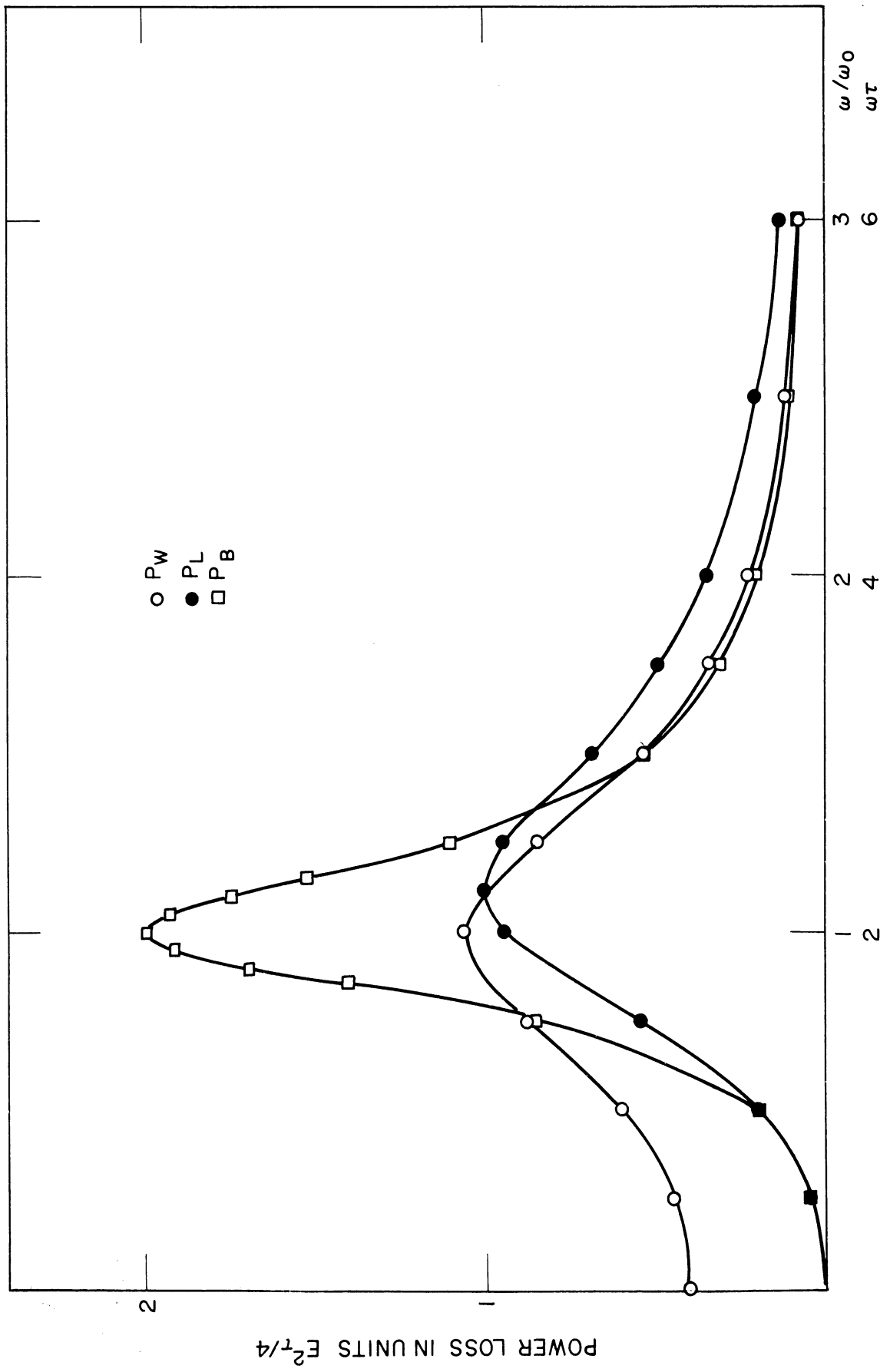


Fig. 4. $\omega_0\tau = 2$.

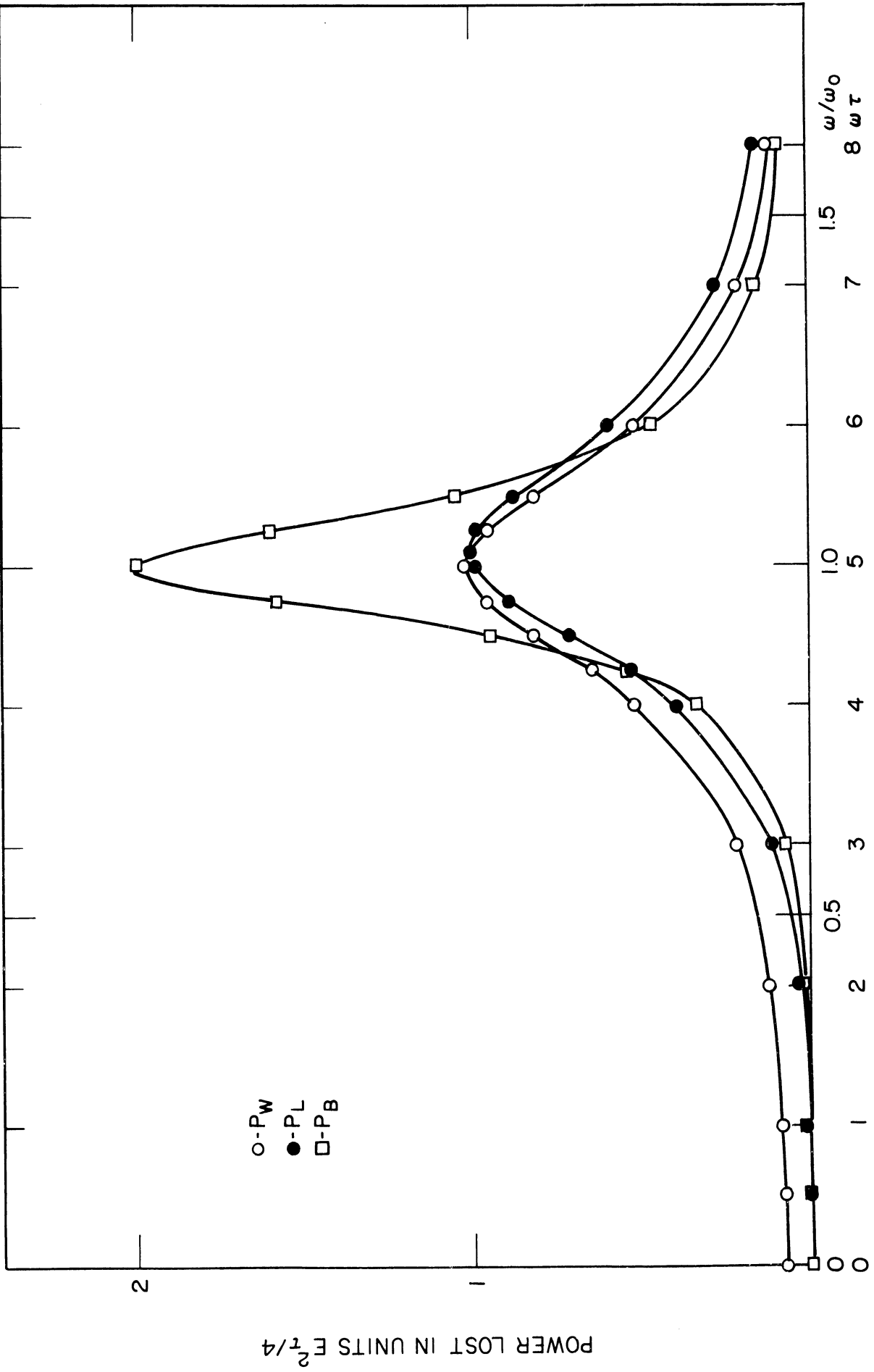


Fig. 5. $\omega_0 T = 5$.

