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A MODERATELY DENSE LENNARD-JONES GAS

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ABSTRACT

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First and second order density corrections to the transport coefficients of a gas of Lennard-Jones molecules are evaluated numerically. The results are based on the formal kinetic theory development of Snider and Curtiss as later modified by Snider and McCourt. This treatment, in turn, is based on the modification of the Boltzmann equation suggested by Green. This modification is an approximation to the series development of Bogolubov and Hollinger and Curtiss. The numerical methods used in the evaluation of the various integrals are discussed. The effect of three body collisions on the first density correction term is considered approximately through a generalization of the Enskog rigid sphere expression.

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THE TRANSPORT PROPERTIES OF A MODERATELY DENSE LENNARD-JONES GAS

The theory of transport phenomena based on the Boltzmann equation applies only to low density gases composed of monatomic molecules. It is limited by the basic assumptions of the Boltzmann equation which completely ignore three body collisions and require that the molecular dimensions be small in comparison with the mean free path. In order to extend the theory to higher densities the Boltzmann equation must be appropriately modified.

The first attempt to describe the transport properties of dense gases is due to Enskog[1] who studied an idealized system of rigid spherical molecules. His treatment involves a modification of the original Boltzmann equation to include two separate effects. He recognized that due to the finite size of the interacting molecules momentum and energy are instantaneously transferred between molecular centers on collision. Secondly, he allowed, approximately, for the effect of three body collisions by introducing the equilibrium radial distribution function Y evaluated at impact separation to describe the effect of shielding of a colliding pair by a third molecule. For rigid spheres Y at the impact separation is given by the density expansion

$$Y = 1 + \left(\frac{C}{B}\right) n + \cdots \tag{1}$$

where B and C are respectively the second and third virial coefficients, and n is the number density.

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[1] D. Enskog, Kgl. Svenska Vetenskapsakad. Handl <u>63</u>, No. 4 (1922). See also Molecular Theory of Gases and Liquids, J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, page 634 (John Wiley, New York, 1954).

The more realistic case of a gas of soft molecules has been discussed by a number of authors, including Bogolubov[2], Green[3], and Hollinger and Curtiss[4]. These authors separately developed identical contributions to the Boltzmann collision integral describing collisional transfer. In the limiting case of rigid spheres, these terms are identical with the Enskog result when three body effects are ignored, by setting Y equal to unity. Bogolubov, and Hollinger and Curtiss have developed in addition a term describing the effect of three body collisions. Both types of corrections to the Boltzmann collision integral lead to contributions of order n and higher in the density expansions of the transport coefficients.

The three body collision correction term mentioned above is quite complicated and has not yet been used in a practical calculation. It is possible on the basis of the Enskog theory, however, to approximate the effect of three body collisions. The Enskog three body corrections to the transport coefficients appear in the linear and higher terms of the density expansion. The corrections of order n are

$$- \lambda^{(o)} \, n \, \left(c/_B \right) \tag{2}$$

for the coefficient of thermal conductivity and

$$- \eta^{(o)} \, n \, \left(c/_B \right) \tag{3}$$

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[2] N. Bogolubov, J. Phys. (U.S.S.R.) <u>10</u>, 265 (1946).

[3] H. S. Green, Molecular Theory of Fluids (North Holland Publishing Co., Amsterdam 1952).

[4] H. B. Hollinger and C. F. Curtiss, J. Chem. Phys. <u>33</u>, 1386 (1960).

for the coefficient of shear viscosity where $\lambda^{(o)}$ and $\eta^{(o)}$ are the constant terms in the density expansions and B and C are respectively the second and third rigid sphere virial coefficients. In his early treatment of the problem, Enskog suggested, with considerable success, an intuitive method of applying the rigid sphere results to the soft potential case. An essential point in Enskog's intuitive modification is the evaluation of Y in terms of the equation of state through the relation[5]

$$Y = \frac{1}{n \, b_o'} \left[\frac{1}{n \, k} \left(\frac{\partial p}{\partial T} \right) - 1 \right] \tag{4}$$

where b_o' is a function of the temperature, T. It is easily shown that if Y is to approach unity in the limit $n \to 0$, b_o' must be taken to be

$$b_o' = \frac{d}{dT} (T B) \tag{5}$$

It then follows that the Enskog relation is

$$Y = 1 + n \frac{d}{dT} (T C) / \frac{d}{dT} (T B) + \cdots \tag{6}$$

A comparison of this result with the rigid sphere expression, Eq. 1, then suggests that the results of the present treatment may be corrected approximately for the effects of three body collisions by replacing the ratio C/B in the rigid sphere expressions,

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[5] See Molecular Theory of Gases and Liquids, J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird (John Wiley, New York, 1954), p. 649.

Eqs. 2 and 3, by the ratio

$$\frac{d}{dT}(TC) \Big/ \frac{d}{dT}(TB) \tag{7}$$

evaluated for the soft potential. A more rigorous generalization of the Enskog treatment to the soft molecule case will be discussed in a later paper.

Livingston and Curtiss[6] have investigated the question of three body corrections to the rigid sphere transport coefficients with more rigor than did Enskog. They have obtained further linear corrections by considering the perturbation of the radial distribution function. These corrections, however, are not easily generalized to the soft potential case.

On the basis of Green's collisional transfer modification of the Boltzmann equation, Snider and Curtiss[7] developed expressions for the corrections to the transport coefficients. . The explicit expressions for these collisional transfer density corrections have been considered further by Snider and McCourt[8]. They succeeded in simplifying appreciably the form of the expressions and showed that certain combinations of the integrals can be evaluated immediately in terms of the second virial coefficient and its derivatives. For a purely repulsive inverse power potential the remaining integrals

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[6] P. M. Livingston and C. F. Curtiss, Phys. of Fluids, 4, 816 (1961).

[7] R. F. Snider and C. F. Curtiss, Phys. of Fluids, 1, 122 (1958); 3, 903 (1960).

[8] R. F. Snider and F. R. McCourt, Phys. of Fluids, 6, 1020 (1963).

were evaluated by an interesting expansion about the rigid sphere

case as a limit.

In the present paper the evaluation of the density corrections to the transport coefficients

is considered for a potential function including an attractive as

well as a repulsive term. Specifically the calculations are based

on the Lennard-Jones potential defined by

$$\varphi_{(R)} = \epsilon \, f\left(^{R}/_{\sigma}\right) \qquad (8)$$

where

$$f(z) = 4\left[x^{-12} - x^{-6} \right] \qquad (9)$$

r is the separation distance of the molecules, ϵ is the depth

of the potential minimum, and σ is the separation distance at

which the potential is zero.

The basic problem is the numerical evaluation of certain triple

integrals, the integrands of which depend on functions also obtained

by numerical integration.

1. THEORY

The expressions for the coefficients of thermal conductivity,

shear and bulk viscosity obtained by Snider and McCourt can be

written in the form

$$\lambda = \frac{-n\,k}{4}\left(\frac{2\,kT}{m}\right)^{1/2} a_1\left[5 - nT^2\frac{d^2 B}{dT^2} - \frac{4\pi}{3}n\sigma^3(N_\lambda - T_\lambda)\right] \qquad (10)$$

$$+ \frac{n^2\,k\,\sigma^4}{3}\left(\frac{\pi\,kT}{m}\right)^{1/2}\left(H_\lambda + R_\lambda - I_\lambda \right)$$

$$\eta = (1/2)\, n\, k\, T\, b_0 \left[1 - \frac{4\pi^{1/2}}{15} n\, \sigma^3\, N_\eta \right]$$

$$+ \frac{2\, n^2 \sigma^4}{15} (\pi m k T)^{1/2} (H_\eta + R_\eta) \tag{11}$$

and

$$\varkappa = \frac{n^2 k T}{4} c_2 \left(T^2 \frac{d^2 B}{d T^2} + 2T \frac{d B}{d T} \right)$$

$$+ \frac{2\, n^2 \sigma^4}{9} (\pi m k T)^{1/2} (H_\varkappa + R_\varkappa) \tag{12}$$

in which m is the mass of a molecule, k is the Boltzmann constant, T is the temperature, and a_1, b_0 and c_2 are defined by

$$- 8\, n^2 \sigma^2 \left(\frac{\pi k T}{m} \right)^{1/2} \Omega^{(2,2)*} a_1 = \frac{15}{4} \left(\frac{2 k T}{m} \right)^{1/2} n \left[1 + n B - \frac{4 n \sigma^3}{3 \pi^{1/2}} F_\lambda \right] \tag{13}$$

$$- 8\, n^2 \sigma^2 \left(\frac{\pi k T}{m} \right)^{1/2} \Omega^{(2,2)*} b_0 = - 5 n \left[1 + n B - \frac{4 n \sigma^3}{15 \pi^{1/2}} F_\eta \right] \tag{14}$$

and

$$- 4\, n^2 \sigma^2 \left(\frac{\pi k T}{m} \right)^{1/2} \Omega^{(2,2)*} c_2 = \frac{2\, n^2 \sigma^3}{3 \pi^{1/2}} F_\varkappa \tag{15}$$

In these expressions, B is the second virial coefficient, $\Omega^{(2,2)*}$ is the usual dimensionless viscosity cross-section, and N_λ, T_λ, H_λ, etc. are triple integrals which are discussed in detail later.

The expressions for the transport coefficients can also be written in the form of polynomials in the density,

$$\lambda = \lambda^{(o)}\left[1 + n B_\lambda + n^2 C_\lambda \right] \tag{16}$$

$$\eta = \eta^{(o)}\left[1 + n B_\eta + n^2 C_\eta \right] \tag{17}$$

$$\mu = \eta^{(o)}\left[n^2 C_\varkappa \right] \tag{18}$$

where $\lambda^{(0)}$ and $\eta^{(0)}$ are the coefficients in the limit of a dilute gas, and the B_λ, B_η, C_λ, C_η and $C_\varkappa$ are the "transport property virial coefficients" given by

$$B_\lambda/\sigma^3 = B_\lambda^* = \frac{2\pi}{3}B^* - \frac{2\pi}{15}B_2^* - \frac{4}{15}(\pi^{1/2})F_\lambda - \frac{4}{15}\pi^{1/2}(N_\lambda - T_\lambda) \tag{19}$$

$$C_\lambda/\sigma^6 = C_\lambda^* = -\frac{4\pi^2}{45}B^*B_2^* - \frac{8\pi^{3/2}}{45}B^*(N_\lambda - T_\lambda) \tag{20}$$

$$\frac{8\pi^{1/2}}{45}B_2^*F_\lambda + \frac{16}{45}F_\lambda(N_\lambda - T_\lambda) + \frac{64\pi}{225}\Omega^{(2,2)*}\left[H_\lambda + R_\lambda - I_\lambda\right]$$

$$B_\eta/\sigma^3 = B_\eta^* = \frac{2\pi}{3}B^* - \frac{4}{15}(\pi^{1/2})F_\eta - \frac{4}{15}\pi^{1/2}N_\eta \tag{21}$$

$$C_{\eta}/\sigma^6 = C_\eta^* = -\frac{8\pi^{3/2}}{45} B^+ N_\eta + \frac{16}{225} F_\eta N_\eta + \frac{32\pi}{75} \Omega^{(2,2)*}[H_\eta + R_\eta] \qquad (22)$$

and

$$C_{H}/\sigma^6 = C_H^* = -\frac{4\pi^{1/2}}{45} F_H [2B_1^* + B_2^*] + \frac{32\pi}{45} \Omega^{(2,2)*}[H_H + R_H] \qquad (23)$$

where

$$F_\eta = \frac{15}{2} F_\lambda + \frac{5\pi^{3/2}}{12}[7B_1^* + 2B_2^*] \qquad (24)$$

$$F_H = -\frac{\pi^{3/2}}{12}[10B_1^* + 11B_2^* + 2B_3^*] \qquad (25)$$

$$T_\lambda = \frac{\pi^{1/2}}{6}[7B_1^* + 2B_2^*] \qquad (26)$$

$$N_\eta = \frac{3}{2} N_\lambda + \frac{\pi^{1/2}}{4}[5B^* + 2B_1^*] \qquad (27)$$

$$H_\eta + R_\eta = \frac{3}{2}[H_\lambda + R_\lambda] - \frac{1}{2}[H_H + R_H] \qquad (28)$$

and

$$B^* = B/(\tfrac{2}{3}\pi\sigma^3) \qquad (29)$$

$$B_\nu^+ = T^{*\nu} \left(\frac{d^\nu}{dT^{*\nu}} \right) B^* \quad ; \quad \nu = 1, 2, 3 \tag{30}$$

In summary, to determine the transport coefficients in the present approximation, five basic integrals F_λ, N_λ, I_λ, $(H_\lambda + R_\lambda)$ and $(H_\kappa + R_\kappa)$ are required. Explicit expressions for these quantities are given by Snider and McCourt and involve triple integrations over the variables λ, g and ω, where λ is the relative separation of the two colliding molecules, g is the magnitude of their relative velocity and $\eta - \omega$ is the angle between the associated vectors. These variables define a collisional trajectory and a point along this trajectory. As a result of the symmetry, the integrals can be written as functions only of that portion of relative position-velocity space defined by points on the incoming portion of the trajectories. It is convenient, in the numerical evaluation of the integrals to change variables from (ω, g) to (g_0, S_0) where g_0 is the initial relative velocity in a collision and S_0 is the distance of closest approach of the particles. The variables (g_0, S_0) uniquely describe a trajectory and the remaining variable r fixes the position on this trajectory. Before writing these expressions it is convenient to introduce the dimensionless variables

$$\lambda^* = \lambda/\sigma \tag{31}$$

$$S^* = S/\sigma \tag{32}$$

$$s_o^* = s_o/\sigma \tag{33}$$

$$T^* = kT/\epsilon \tag{34}$$

$$q_o^* = \sqrt{\frac{A}{4\epsilon}}\, q_o \tag{35}$$

From this point on the explicit expressions are written in terms
of these dimensionless variables but for typographical convenience
the asterisks are omitted. In terms of these dimensionless
variables the explicit expressions for the triple integrals are

$$F_\lambda = \frac{4P}{5 T^{5/2}} \iiint exp\left(\frac{-q_o^2}{T}\right) q_o\, s_o^2\, f'(\lambda)\, [q_o^2 - f(s_o)]^{1/2}$$

$$\times \frac{H(q_o, s_o)}{G(q_o, s_o, \lambda)}\left[G(q_o, s_o, \lambda)\left\{ 2Y + cos(2\omega)\, sin(2\rho) \right.\right.$$

$$\left. - X\, sin(2\omega)\, sin(2\rho) + Y\, cos(2\omega)\, cos(2\rho)\right\}$$

$$+ s_o\left\{ q_o^2 - f(s_o)\right\}^{1/2}\left\{ cos(2\omega)\, cos(2\rho) - X\, sin(2\omega)\, cos(2\rho)\right.$$

$$\tag{36}$$

$$\left.\left. - Y\, cos(2\omega)\, sin(2\rho)\right\}\right]\, dq_o\, ds_o\, d\lambda$$

$$N_\lambda = \frac{2}{T} \frac{7}{2} \iiint \exp\left(\frac{-g_0^2}{T}\right) g_0^3\, s_0\, f'(r)\, r^2\, \frac{H(g_0, s_0)}{G(g_0, s_0, r)}$$

$$\times \left[1 + \cos(2\omega)\cos(2\rho)\right] dg_0\, ds_0\, dr \tag{37}$$

$$I_\lambda = \frac{4}{T^3} \iiint \exp\left(\frac{-g_0^2}{T}\right) \left\{g_0^2 - f(s_0)\right\}^{1/2} \frac{H(g_0, s_0)}{G(g_0, s_0, r)} f(r)$$

$$\times r\, s_0^2\, g_0\, X\, dg_0\, ds_0\, dr \tag{38}$$

$$H_\lambda + R_\lambda = \frac{1}{T^3} \iiint \exp\left(\frac{-g_0^2}{T}\right) r^2\, s_0^2\, g_0\, f'(r) \left\{g_0^2 - f(s_0)\right\}^{1/2}$$

$$\times \frac{H(g_0, s_0)}{G(g_0, s_0, r)} \left\{ 2 X (1 + \cos(2\omega)\cos(2\rho)\right. \tag{39}$$

$$\left. + 2\sin(2\omega)\cos(2\rho) - Y\sin(2\omega)\sin(2\rho)\right\} dg_0\, ds_0\, dr$$

$$H_x + R_x = \frac{1}{T^3} \iiint \exp\left(\frac{-g_0^2}{T}\right) \left\{g_0^2 - f(s_0)\right\}^{1/2} \frac{H(g_0, s_0)}{G(g_0, s_0, r)}$$

$$\times g_0\, r^2\, s_0^2\, f'(r)\, X\, dg_0\, ds_0\, dr \tag{40}$$

in which $f'(\lambda)$ is the derivative of $f(x)$ and

$$H(q_0, s_0) = q_0^2 - f(s_0) - \tfrac{1}{2} s_0 f'(s_0) \tag{41}$$

$$G(q_0, s_0, \lambda) = \left\{ \lambda^2 [q_0^2 - f(\lambda)] - s_0^2 [q_0^2 - f(s_0)] \right\}^{1/2} \tag{42}$$

$$\rho = s_0 [q_0^2 - f(s_0)]^{1/2} \int_{s_0}^{\lambda} \frac{ds}{s\, G(q_0, s_0, s)} \tag{43}$$

$$Y = \frac{-q_0^4}{s_0 [q_0^2 - f(s_0)]^{1/2}} \int_{s_0}^{\lambda} \frac{s\, ds}{G(q_0, s_0, s)} \tag{44}$$

$$X = \frac{q_0^2}{s_0 [q_0^2 - f(s_0)]^{1/2}} \int_{s_0}^{\infty} \left\{ \frac{s}{G(q_0, s_0, s)} - \frac{1}{q_0} \right\} ds \tag{45}$$

$$\frac{-q_0}{[q_0^2 - f(s_0)]^{1/2}}$$

$$\omega = -s_0 [q_0^2 - f(s_0)]^{1/2} \int_{s_0}^{\infty} \frac{ds}{s\, G(q_0, s_0, s)} \tag{46}$$

The integrations in equations (36), (37), (38), (39) and (40) are limited to regions of the relative position-velocity space corresponding to non-bound trajectories. In the theory, this results from the use of the molecular chaos assumption to derive the Boltzmann equation. The molecular chaos assumption requires that two molecules in collision have been separated in their past history. Thus, if the treatment is limited to binary collisions, the molecular

chaos assumption cannot be used in the bound state region. Numerically, this restriction arises because the integrands of those integrals which cannot be reduced to the second virial coefficient or its temperature derivatives become undefined in the bound state region. There is a question as to whether to retain the full second virial coefficient or limit it also to non-bound state contributions. The situation is further complicated by the fact that such terms arise in the treatment in two ways. First, the second virial coefficient appears in the expression for the equilibrium pressure in which case the full coefficient must surely be used. Secondly, certain molecular integrals reduce to the integral representation of the second virial coefficient. It is in the latter case that the difficulty arises. Since the contributions to the transport coefficients due to the bound state region have not been treated in a satisfactory theoretical manner, it is difficult at this time to decide how the situation should be resolved. In this paper, the full second virial coefficient is used wherever it appears explicitly.

In the non-bound region of the relative position-velocity space, the limits on the integration variable r are ζ_0 to infinity. The limits of integration on q_0 and ζ_0 are more complicated. In this case the range of integration is restricted as indicated in figure 1. Region I is excluded from the integration since here the total energy which is measured q_0^2 is less than the potential energy given by $f(\zeta_0)$. Region II is excluded since it is the region of bound states. Points along the limiting curve a represent head on collisions where there is no rotational kinetic energy. Points near

the boundary curve c represent trajectories in which the particles approach each other and then orbit a large number of times before finally separating. These points correspond to collisions where g_o^2 is slightly less than the maximum in the effective potential energy curve as illustrated in figure 2. Points near curve b also represent an orbiting situation. However, in this case g_o^2 is slightly greater than the maximum in the effective potential energy curve. After orbiting for some time, the particles in this case fall together through the minimum in the effective potential energy, then go back out for a second long period of orbiting before they finally separate. In both orbiting situations the trajectory becomes nearly circular (i.e., the radial velocity becomes nearly zero) at a value of r corresponding to the maximum in the effective potential energy curve. From figure 1 it is seen that for values of g_o less than a critical value the integration over S_o in (36), (37), (38), (39) and (40) must be carried out in two parts. The integration is first from a to b , then from c to infinity. For values of g_o greater than the critical value the range of the variable S_o extends continuously from a to infinity.

The integrals ρ , Υ , X , and ω are closely related to the integrals which give the time elapsed during collision and the total angle of deflection. The quantity $G(g_o, S_o, S)$ which appears in the denominator of the integrand can easily be shown to be

$$S \, g_r (S)$$

where g_r is the magnitude of the radial component of the velocity.

At a turning point g_f is zero and thus there is a pole in the integrand of ρ , Y , X and ω at $f = f_o$. In general this pole causes no difficulty. However, for values of g_o and f_o corresponding to points on either the curves b or c and when f has the value corresponding to the radial separation at the maximum in the effective potential curve, the orbit is circular and both g_f and its time derivative are zero. This is sufficient to cause divergence of the integrals ρ , Y , X , and ω on the curves b and c . Fortunately the divergence of these quantities does not effect the absolute convergence of the integrals defined by (36), (37), (38), (39) and (40). This is ensured by the presence of the factor $H(g_o, f_o)$. It does, however, introduce computational difficulties and it is convenient in the f_o integration, for values of g_o below the critical value, to integrate from a to $b - \delta_1$, and from $c + \delta_2$ to infinity where δ_1 , and δ_2 are small, adjustable parameters. By numerical experimentation, it was found that taking $\delta_1 = 10^{-5}(b-1)$ and $\delta_2 = 10^{-3}$ essentially eliminates the difficulty in the evaluation of the triple integrals. Again a minor difficulty was encountered due to the presence of a pole in the integration at $n = f_o$ due to the factor $G(g_o, f_o, n)$. This was treated in the same manner as the poles in the integrals (43) - (46). The details of the integration methods are discussed below.
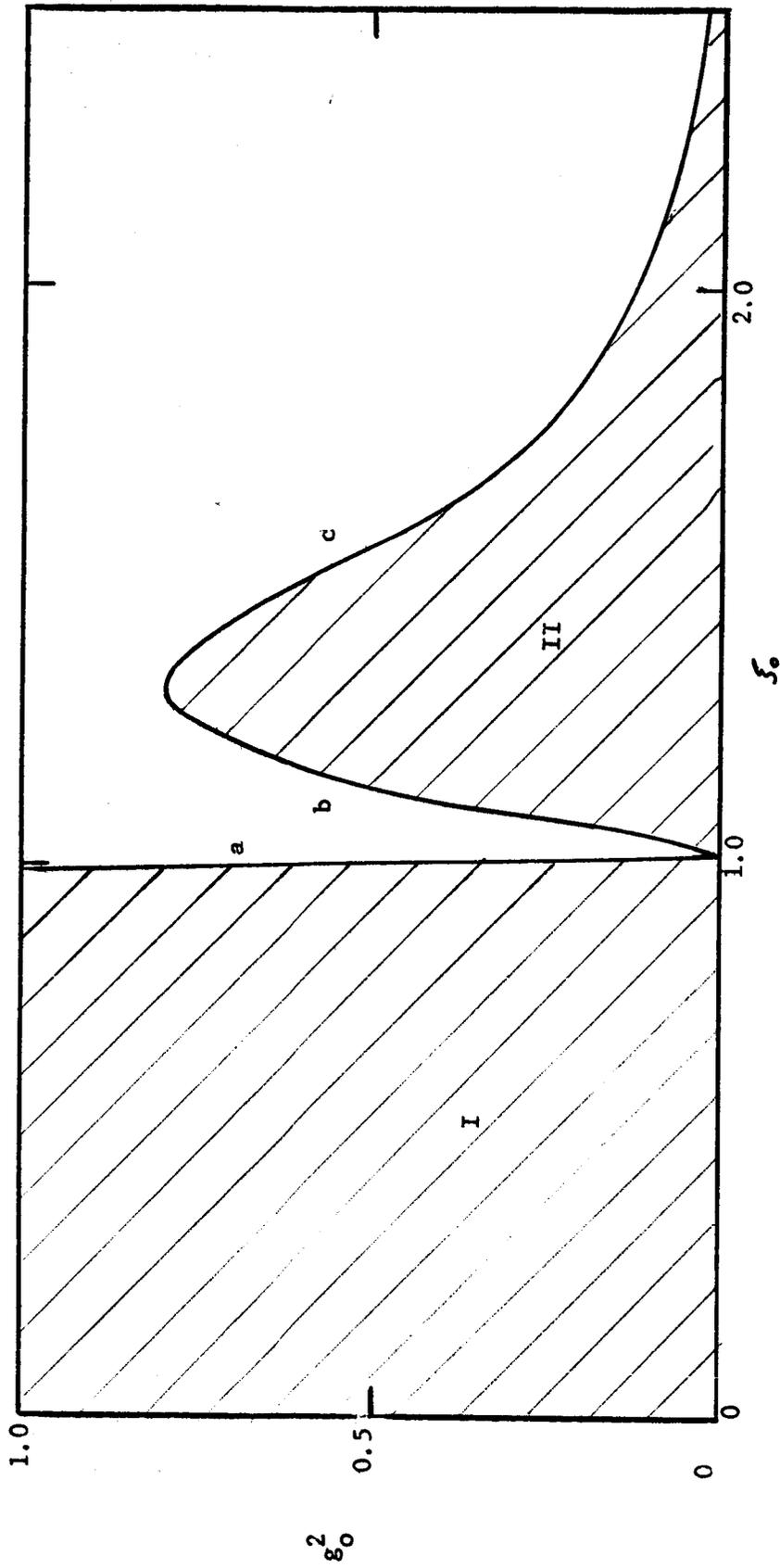
Fig. 1

The integration over (g_o^2, ξ_o) is restricted to the region outside the shaded area.
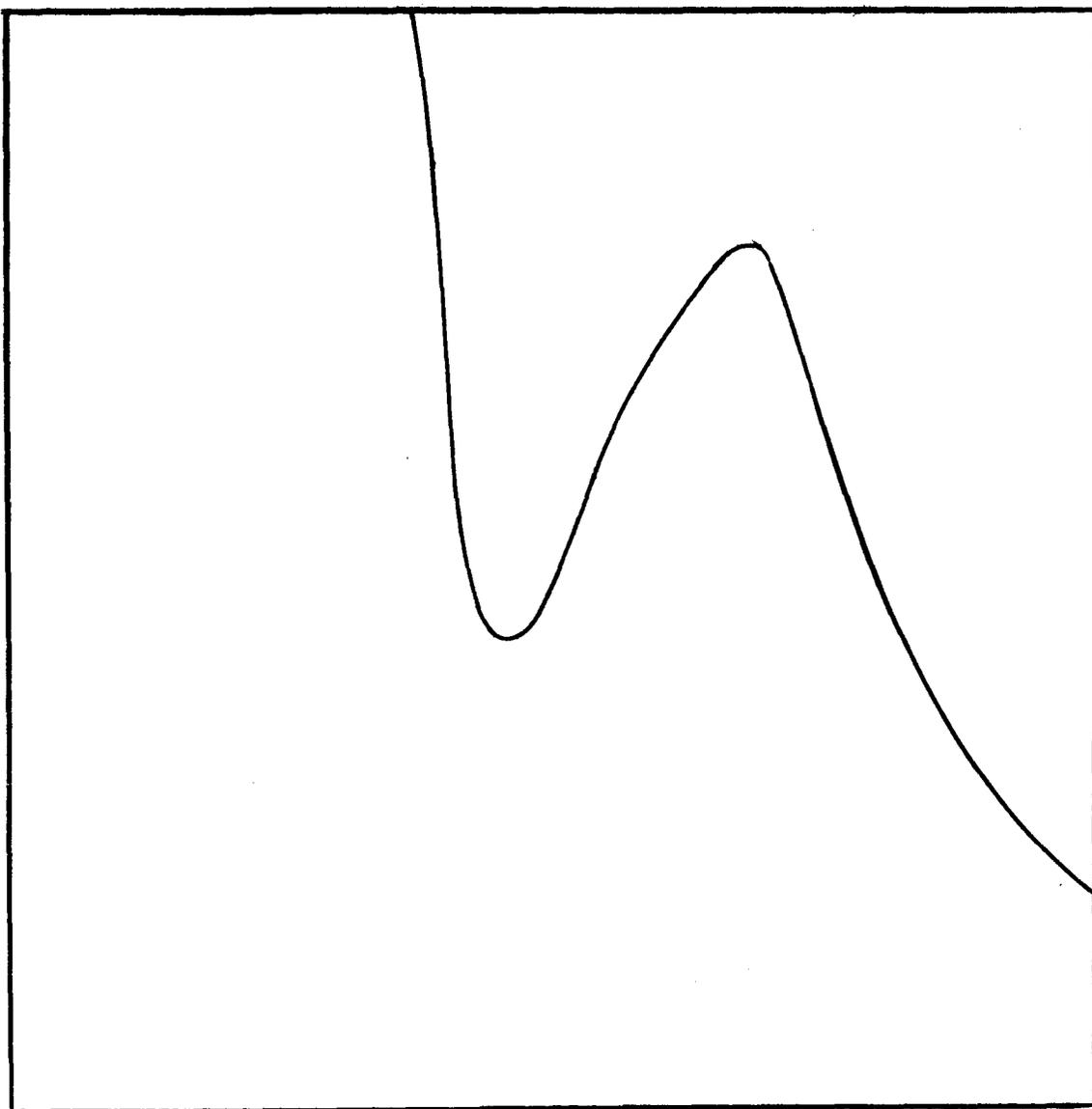
Fig. 2

The effective potential function, $f(\lambda) + \frac{s_o^2}{\lambda^2}\left[g_o^2 - f(s_o)\right]$
for an orbiting angular momentum

2. NUMERICAL METHODS

Since the integrals (36) - (40) are similar in form, it is convenient to describe the numerical method used to compute a typical quantity

$$
\mathcal{F} = \iiint \mathcal{F}^{(3)}(g_o, s_o, z) \, dz \, ds_o \, dg_o \tag{47}
$$

The integration can be represented in the following manner

$$
\mathcal{F} = \int_0^\infty \mathcal{F}^{(1)}(g_o) \, dg_o \tag{48}
$$

where

$$
\mathcal{F}^{(1)}(g_o) = \int \mathcal{F}^{(2)}(g_o, s_o) \, ds_o \tag{49}
$$

in which

$$
\mathcal{F}^{(2)}(g_o, s_o) = \int_{s_o}^\infty \mathcal{F}^{(3)}(g_o, s_o, z) \, dz \tag{50}
$$

It is noted that in the general case the integrand $\mathcal{F}^{(3)}(g_o, s_o, z)$ depends on the functions (43) - (46). These quantities must also be determined by numerical integration.

With the definitions

$$
I_{(1)}(g_o, s_o) = \int_{s_o}^\infty \frac{ds}{s \, G(g_o, s_o, s)} \tag{51}
$$

$$I_{(2)}(g_0, s_0, \pi) = \int_\pi^\infty \frac{ds}{s \, G(g_0, s_0, s)} \qquad (52)$$

$$I_{(3)}(g_0, s_0) = \int_{s_0}^\infty \frac{[s \, g_0 - G(g_0, s_0, s)]}{g_0 \, G(g_0, s_0, s)} \, ds \qquad (53)$$

and

$$I_{(4)}(g_0, s_0, \pi) = \int_\pi^\infty \frac{[s \, g_0 - G(g_0, s_0, s)]}{g_0 \, G(g_0, s_0, s)} \, ds \qquad (54)$$

the integrals ρ , Y , X and ω can be rewritten in the form

$$\rho(g_0, s_0, \pi) = s_0 \, [g_0^2 - f(s_0)]^{1/2} \left\{ I_{(1)}(g_0, s_0) - I_{(2)}(g_0, s_0, \pi) \right\} \qquad (55)$$

$$Y(g_0, s_0, \pi) = \frac{-g_0^2}{s_0 \, [g_0^2 - f(s_0)]^{1/2}} \left\{ I_{(3)}(g_0, s_0) \right.$$

$$\left. - I_{(4)}(g_0, s_0, \pi) + \frac{\pi - s_0}{g_0} \right\} \qquad (56)$$

$$X(g_0, s_0) = \frac{g_0^2}{s_0 \, [g_0^2 - f(s_0)]^{1/2}} \left\{ I_{(3)}(g_0, s_0) - \frac{s_0}{g_0} \right\} \qquad (57)$$

and

$$\omega(g_o, s_o) = -s_o \left[g_o^2 - f(s_o) \right]^{1/2} I_{(4)}(g_o, s_o) \qquad (58)$$

The integrals I_1 and I_3 are independent of λ whereas I_2 and I_4 depend on all three variables g_o, s_o, λ . The values of I_2 and I_4 were required at each of the quadrature points λ_i' used in evaluating (50). A typical integral from λ_i' to infinity was computed by summing the contributions from each interval $(\lambda_j', \lambda_{j+1}')$ $j > i$,

$$\int_{\lambda_i'}^{\infty} = \int_{\lambda_i'}^{\lambda_{i+1}'} + \cdots \int_{\lambda_N}^{\infty} \qquad (59)$$

where λ_N is the largest pivotal point. The individual terms on the right hand side of (59) were expressed as integrals from -1 to 1 and were evaluated with Gauss' quadrature formula[9]. In the evaluation of each of the integrals, the 16 point Gauss formula was used. To obtain I_1 and I_3, integrals from s_o to λ_1 are required. Since the integrands in this case have a pole at the lower limit it is no longer possible to use the Gauss formula. However, introducing a simple change of variable the integrals can be expressed in the form

$$\int_{-1}^{1} \frac{f_1(y)}{(1-y^2)^{1/2}} dy \qquad (60)$$

where the pole originally at s_o is now at the point $y = -1$, and the function $f_1(y)$ is finite and well behaved throughout the

range of integration. Under these conditions the numerical integration is tractable and can be carried out by use of a quadrature formula due to Mehler[9],

$$\int_{-1}^{1} \frac{f(y)}{(1-y^2)^{1/2}} dy = \frac{\pi}{N} \sum_{i=1}^{N} f_i \left[\cos \frac{(2i-1)\pi}{2N} \right] \qquad (61)$$

This is a particular case of a more general quadrature in which the weight function has the form

$$w(y) = (1-y)^\alpha (1+y)^\beta \qquad (62)$$

where α and β are any numbers greater than -1. It is seen that the usual Gauss formula results on setting $\alpha = \beta = 0$ In the evaluation of the integrals I_1 and I_3, 16 points were used in the Mehler integration.

As pointed out earlier the integrand in (50) has a pole at $\lambda = S_0$. In order to obtain accurate results both Mehler and Gauss formulae were employed, the division point being arbitrarily chosen at $\lambda = 2 S_0$. In the Mehler integration 32 points were used and in the Gauss integration 16 points were used. The range of the variable in the integral (49) has been discussed in Section 1. Depending on whether g_0 is less or greater than the critical value we require

$$\int_a^{b-\delta_1} \mathcal{F}^{(2)}(g_0, S_0) dS_0 + \int_{c+\delta_2}^{\infty} \mathcal{F}^{(2)}(g_0, S_0) dS_0 \qquad (63)$$

[9] Z. Kobal, Numerical Analysis (John Wiley, New York, 1961).

or

$$\int_a^\infty \mathcal{T}^{(2)}(q_0, s_0)\, ds_0 \tag{64}$$

After appropriate change of variable, each integral can be expressed in the form

$$\int_{-1}^{1} f_2(y)\, dy \tag{65}$$

They were then evaluated using a 16 point Gauss quadrature.

The integral (48) may be expressed as

$$\int_0^\infty e^{-x} f_3(x)\, dx \tag{66}$$

which can be approximated by the summation

$$\sum_{n=1}^{M} w_n\, f_3(x_n) \tag{67}$$

where the points x_n are the zeros of the M order Laguerre polynomial $L_M(x)$. The weight coefficients w_n are given by

$$w_n = \frac{1}{x_n}\left[\frac{M!}{L'_M(x_n)}\right]^2 \tag{68}$$

Values of x_n and w_n are tabulated for a wide range of M by Rabinowitz and Weiss[10]. In the evaluation of these integrals, the number of Laguerre points M was taken to be 48. It was found, however, that in each case the function $f(x)$ decreased sufficiently rapidly with x that it was necessary to retain only the first 18 terms in the sum (67).

[10] P. Rabinowitz and G. Weiss, Math. Tab., Wash. 13, 285 (1959).

3. NUMERICAL RESULTS AND CONCLUSIONS

The numerical evaluation of the various integrals has been carried out on a CDC 1604 computer. The evaluation of the two "transport property second virial coefficients", B_η^* and B_λ^* and of the "third virial coefficients" C_η, C_H and C_λ at a particular temperature required 15 to 20 minutes of computing time. For smaller T values, as a result of the factor $\exp(-\frac{g_o^2}{T})$ in (36) - (40), values of g_o below the critical value became increasingly important, and the operating time of the program increased accordingly. These five coefficients were evaluated at six widely spaced values of the reduced temperature. The results are given in the table and illustrated in the figures.

The values of $\mathscr{B}_\eta^*$ and $\mathscr{B}_\lambda^*$ were corrected approximately for the effect of three body collisions in the manner described in the introduction. These "corrected" values are also given in the table and figures.

The effect of pressure on the transport coefficients has been discussed previously by Stogryn and Hirschfelder[11]. Their study is based largely on the effect of stable and metastable bound pairs of molecules. Their results for monatomic gases are also illustrated in the figures. These authors compared their results with experimental measurements of the pressure dependence of the transport coefficients. Their reduced values of the second virial coefficients are indicated in the figures by circles.

Recently, Flynn, Hanks, Lemaire, and Ross[12] have determined the

[11] D. E. Stogryn and J. O. Hirschfelder, J. Chem. Phys., 31, 1531 (1959); 33, 942 (1960).

[12] G. P. Flynn, R. V. Hanks, N. A. Lemaire, and J. Ross, J. Chem. Phys., 38, 154 (1963).

viscosity of He, Ne, Ar, and N_2 as functions of the density at four temperatures. The values of the viscosity second virial coefficient, which they obtained from their measured values, have been converted to reduced values using as potential constants, for He, $\epsilon/k = 10.8$ and $\sigma = 2.57$ A; for Ne, $\epsilon/k = 33.7$ and $\sigma = 2.576$ A ; for Ar, $\epsilon/k = 119.5$ and $\sigma = 3.409$ A; and for N_2, $\epsilon/k = 91.5$ and $\sigma = 3.681$ A. The resulting values of B_η^* are indicated in Fig. 3 by squares.

From the law of corresponding states one would expect the reduced experimental values given in the figures to lie on smooth curves. For this reason, it is probable that the scatter of the points is an indication of the experimental uncertainty. The experimental points in the high temperature region tend to indicate that the correction for the effects of three body collisions is larger than that indicated by the approximate correction used in the present discussion. A more rigorous evaluation of this correction will be discussed in a later paper. The experimental points in the low temperature region indicate that either the correction is of opposite sign or substantial disagreement will remain. This difficulty may be due to the effect of bound pairs of molecules. As indicated in the previous discussion, this problem, which is of more importance at lower temperatures, has not been properly treated in the theoretical development.

Acknowledgment

The computations presented in this paper were carried out on a CDC 1604 computer in the University of Wisconsin Numerical Analysis Laboratory. The authors wish to thank Marion Taylor and Grace Rahjes for their help with the numerical methods and for coding the problem for machine computation.

TABLE OF VALUES OF THE TRANSPORT PROPERTY VIRIAL COEFFICIENTS

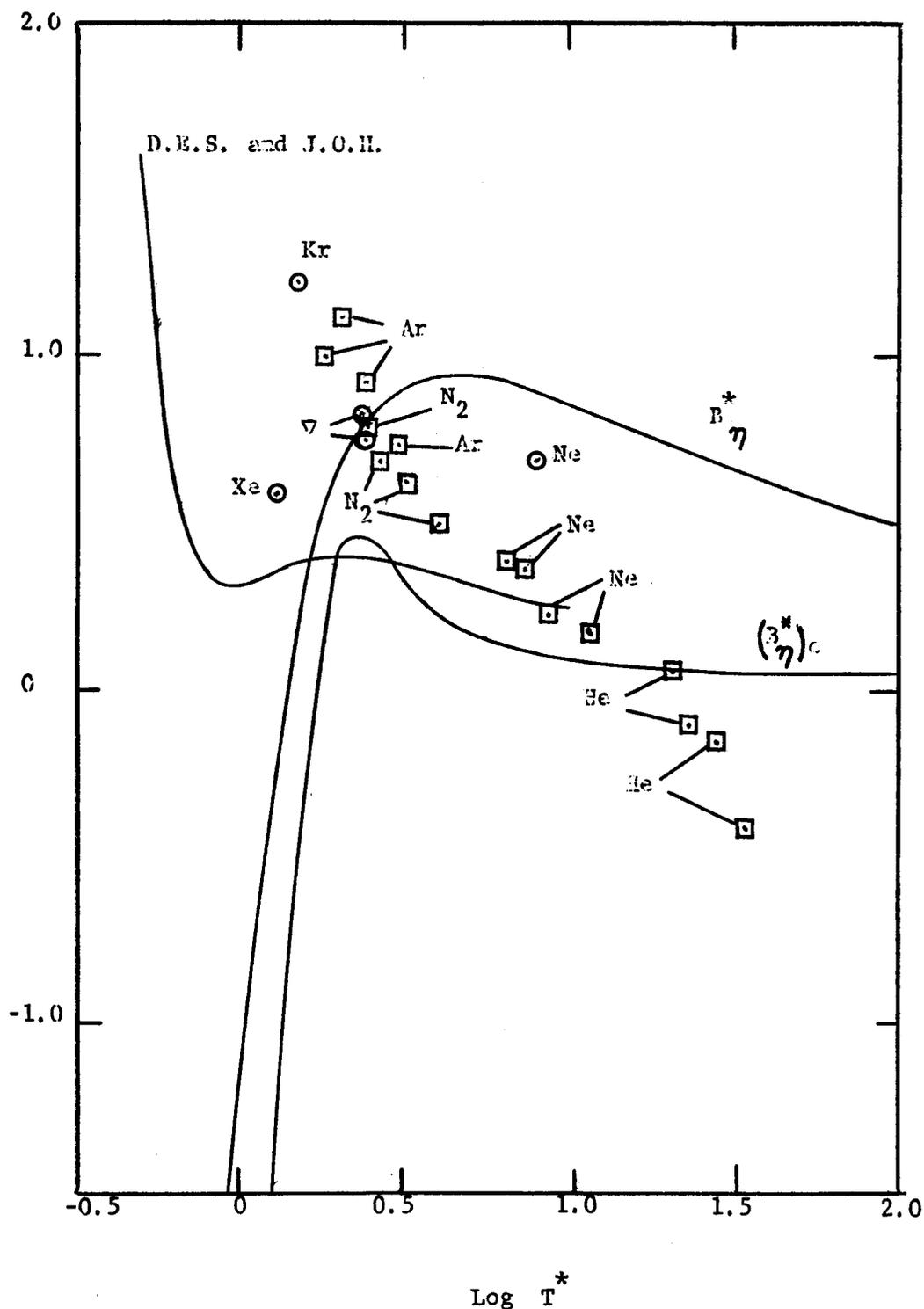| T^*	0.5	1	2	8	30	100
B^*_η	-7.7224	-1.2129	0.6942	0.8991	0.6827	0.5156
B^*_λ	12.8303	4.6662	3.0513	1.6967	1.1169	0.8008
C^*_η	17.24	5.452	3.187	1.502	0.836	0.487
$C^*_\varkappa$	-134.97	12.136	5.636	2.194	1.200	0.697
C^*_λ	-217.56	-1.511	3.420	1.592	0.819	0.459
$(B^*_\eta)_c$		-3.9915	0.4305	0.1005	0.0577	0.0582
$(B^*_\lambda)_c$		1.8876	2.7875	0.8981	0.4919	0.3434

Fig. 3 The reduced "second virial coefficient" for viscosity. The three
curves are a) B_η^*, the quantity computed according to Eq. 21,
b) $(B_\eta^*)_c$, the latter quantity corrected approximately for the effect
of three body collisions, according to Eq. 7, c) values computed by
Stogryn and Hirschfelder[11]. The circles are reduced experimental values
given by Stogryn and Hirschfelder[11]. The squares are based on the
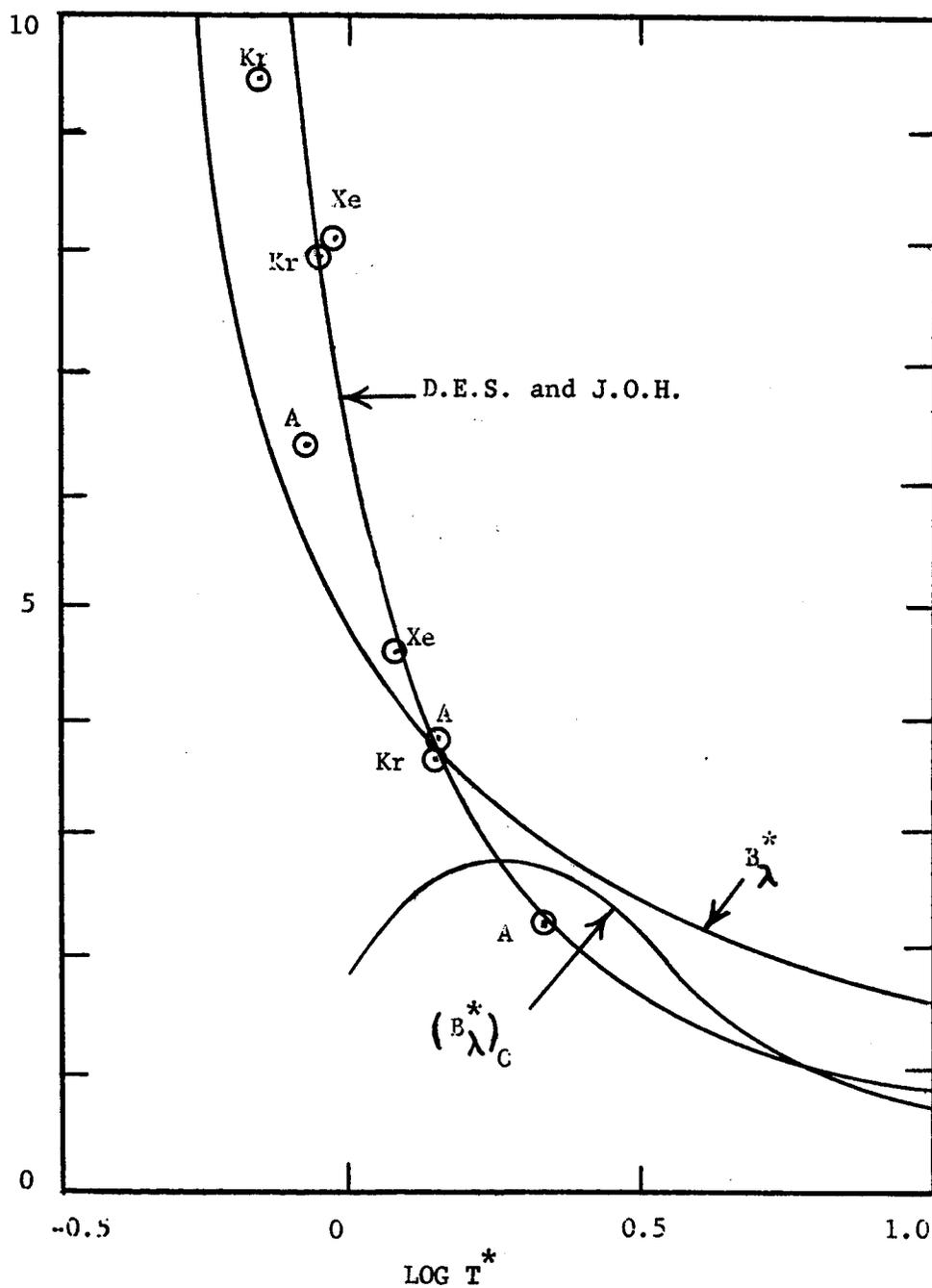experimental values of Flynn, Hanks, Lemaire, and Ross[12].

Fig.4

The reduced "second virial coefficient" for thermal conductivity. The three curves are a) B_λ^* , the quantity computed according to Eq. 19, b) $(B_\lambda^*)_c$, the latter quantity corrected approximately for the effect of three body collisions, according to Eq. 7, c) values computed by Stogryn and Hirschfelder[11]. The points are experimental values.