DETERMINATION OF CORRELATIVE FUNCTIONS FOR DENSE GASES AND LIQUIDS

I. SYSTEM OF RIGID SPHERES

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A new method is suggested of cutting off the Bogolyubov equation chain for distribution functions, based on additive substitution of the variables and yielding a linear equation for the binary correlative function. The physical sense of the equation closely resembles that of the Kirkwood superposition equation but it is superior in that the solution can be obtained in analytical form. Analysis of the equation reveals that if the only forces between the particles are repulsive forces then the binary function always has an oscillating form; if only attractive forces are in effect, the binary function will decrease monotonically with the distance. A solution is obtained for a system of rigid spheres and it is shown that it yields results that are close to those previously obtained by linear solution of the superposition equation.

1. One of the most important statistical methods of calculating the thermodynamic parameters of dense gases and liquids is the Kirkwood method [1], based on termination of an infinite chain of equations for the distribution functions, effected by a multiplicative change of variables. Unfortunately, the so-called "superposition" equations that result from this procedure are integro-differential equations with very strong nonlinearity. Such equations can be solved only by numerical computer integration [2].

We consider below an additive method of changing variables, which leads to linear integral equations. These equations have a great advantage over the superposition equations in that, at least in the simplest cases (for example, in the case of a system of rigid spheres), their solution can be obtained analytically. At the same time, the quantitative difference between the results obtained by multiplicative or by additive change of variable is small, since the physical meaning of both changes is practically the same.

2. We start from the Bogolyubov equations for the distribution function $G_{1,\ldots,s}$ [3]:

$$\nabla_1 G_{1,\ldots,s} + \frac{G_{1,\ldots,s}}{\Theta}\nabla_1 U_{1,\ldots,s} + \frac{1}{v\Theta}\int_V G_{1,\ldots,s+1}\nabla_1\Phi_{1,s+1}\,dr_{s+1} = 0, \quad (1)$$

where $\Theta = kT$, $v = V/N$, V — volume occupied by the system, N — total number of the particles in the system, r_i — radius vector of the i-th particle, ∇_1 — gradient with respect to the coordinates of particle 1; $dr_{s+1} = dx_{s+1}dy_{s+1}dz_{s+1}$, and $U_{1,\ldots,s}$ — energy of interaction between the members of the complex consisting of particles $1,\ldots,s$:

$$U_{1,\ldots,s} = \sum_{1\leqslant i<j\leqslant s}\Phi_{ij}, \quad \Phi_{ij} = \Phi(r_{ij}), \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|,$$
$$\lim_{r_{ij}\to 0}\Phi_{ij} = +\infty, \quad \lim_{r_{ij}\to\infty}\Phi_{ij} = 0. \quad (2)$$

Since $U_{1,\ldots,s}$ depends only on the relative distance r_{ij} between the particles, $G_{1,\ldots,s}$ are also functions of r_{ij} only, and consequently do not depend on the absolute values of r_i.

The distribution functions $G_{1,\ldots,s}$ must usually satisfy three conditions: the normalization condition, the condition of symmetry under permutation of the coordinates of all particles, and the condition of decrease of correlation [3]

$$G_{1,\ldots,s} \to 1, \text{ when all } r_{ij}\to\infty. \quad (3)$$

We impose on $G_{1,\ldots,s}$ one more condition, namely that the particles be impermeable:

$$G_{1,\ldots,s} \to \prod_{1\leqslant i<j\leqslant s}\gamma_{ij}, \quad \gamma_{ij} = \exp[-\Phi_{ij}/\Theta] \to 0,$$
when all $r_{ij}\to 0$,
$$G_{1,\ldots,s} \to \gamma_{kl} f(\mathbf{r}_1,\ldots,\mathbf{r}_s), \quad f \geqslant 0,$$
when all $r_{kl}\to 0$. (4)

This approach of $G_{1,\ldots,s}$ to zero is the consequence of the Gibbs canonical distribution and of the fact that the Born repulsion forces which occur at small distances, are so large (compared with the long-range forces) that a pair of particles in-

teracts via these forces only as if the remaining $N-2$ particles were missing from the system.

3. We note that if r_{12} is large then we get from (3) for the binary function $G_{12} \approx 1 + g_{12}$, where g_{12} is a small addition. To the contrary, if $r_{12} \to 0$, then according to (4) $G_{12} \approx \gamma_{12}$. Combining these two expressions, we obtain $G_{12} = \gamma_{12}(1 + g_{12})$.

We now proceed to the ternary function G_{123}. If the distance between all three particles is large (and consequently the interaction between them is small), then the probabilities of finding the particles 1, 2, 3, at distances r_{12}, r_{13}, and r_{23} from one another can be regarded as independent. Therefore, when r_{ij} is large, we have $G_{123} \approx G_{12}G_{13}G_{23} \approx 1 + g_{12} + g_{13} + g_{23}$. To the contrary, for small r_{ij}, we have $G_{123} \approx \gamma_{12}\gamma_{13}\gamma_{23}$. Combining the two expressions and recognizing that nonlinear effects which are not described by any of the indicated limiting formulas come into play at medium distances, we obtain for the ternary function the expression

$$G_{123} = \gamma_{12}\gamma_{13}\gamma_{23}(1 + g_{12} + g_{13} + g_{23} + g_{123}).$$

Continuing this procedure, we can express the distribution function $G_{1,\ldots,s}$ of order s in terms of the correlative functions $g_{1,\ldots k}$ of order $k \leq s$ in a linear manner. Since, however, we are confining ourselves in the present communication to an analysis of the binary equation only, we shall need for what follows only two formulas:

$$G_{12} = \gamma_{12}(1 + g_{12}),$$

$$G_{123} = \gamma_{12}\gamma_{13}\gamma_{23}(1 + g_{12} + g_{13} + g_{23} + g_{123}). \quad (5)$$

It is necessary to impose on the correlative functions $g_{1,\ldots,s}$ the conditions

$$g_{1,\ldots,s} \to 0 \text{ as } r_{ij} \to \infty \qquad (1 \leqslant i < \ldots \leqslant s) \quad (6)$$

in order to satisfy requirement (3). In addition, the change of variables (5) is possible only when the pair interaction energy Φ_{ij} decreases with increasing distance faster than $1/r_{ij}$, otherwise the integrals in (1) diverge. We shall therefore assume henceforth that the requirement

$$\Phi_{ij} = 0, \qquad \gamma_{ij} = 1 \text{ for } r_{ij} \geqslant R_0 \quad (7)$$

is always satisfied.

4. Let us find now an equation for the correlative function g_{12}. To this end we substitute (5) in (1) and replace γ_{ik} by $\gamma_{ik} = 1 + f_{ik}$. As a result we get

$$\nabla_1 g_{12} - \frac{1}{v}\int_V g_{23}\nabla_1 f_{13}\,dr_3 - \frac{1}{v}\left\{\int_V (1 + g_{12} + g_{13} + g_{23}) f_{23}\nabla_1 f_{13}\,dr_3\right\}$$

$$= \frac{1}{v}\int_V g_{123}\nabla_1 f_{13}\,dr_3 + \int_V g_{123}f_{23}\nabla_1 f_{13}\,dr_3. \quad (8)$$

The expression in the curly brackets of (3) vanishes when $r_{12} \geq 2R_0$, for the presence of the product $f_{13}f_{23}$ under the integral sign causes the integration to be carried out in fact not over the entire infinite space, but over the region where the spheres of radius R_0 intersect (we recall that according to (7) $f_{ij} = 0$ when $r_{ij} \geq 2R_0$). If distances r_{12} between the centers of the spheres are larger than $2R_0$, then the spheres do not overlap and the integration region vanishes. Thus, when $r_{12} \geq 2R_0$ the function g_{12} satisfies the equation

$$\nabla_1 g_{12} - \frac{1}{v}\int_V g_{23}\nabla_1 f_{13}\,dr_3 = \frac{1}{v}\int_V g_{123}\nabla_1 f_{13}\,dr_3. \quad (9)$$

The condition at infinity (6) and Eq. (8), which is specified on the interval $(0, 2R_0)$, constitute the boundary conditions for the function g_{12} defined by (9).

In first approximation, the right half of (9) can be neglected, since

$$\int_V g_{23}\nabla_1\gamma_{13}\,dr_3 \gg \int_V g_{123}\nabla_1\gamma_{13}dr_3 \quad (10)$$

(we recall that $\nabla_1 f_{13} = \nabla_1\gamma_{13}$). Indeed, at large distances, g_{23} is known to exceed g_{123}, and although possibly $g_{23} \approx g_{123}$ at small distances, the presence under the integral sign of a factor g_{13} which decreases exponentially with r_{13} makes the difference between g_{23} and g_{123} negligible. We note that the requirement that g_{123} be small in an integral sense is much weaker than the requirement that g_{123} be small compared with g_{23} directly.

If we drop the right half of (9) and integrate the resultant homogeneous equation with respect to r_1 and the angle coordinates, we obtain

$$\psi(r) = \frac{2\pi}{v}\left\{\int_0^r \psi(t)\,dt \int_{r-t}^{r+t} f(\tau)\,\tau d\tau + \int_r^\infty \psi(t)\,dt \int_{t-r}^{t+r} f(\tau)\,\tau d\tau\right\}, \quad (11)$$

where $r = r_{12}$ and $\psi(r) = rg(r)$. Analogously, neglecting the right half in (8), we get

$$0 \leqslant r_{12} \leqslant 2R_0,$$

$$\Psi_{12} = \nabla_1 g_{12} - \frac{1}{v}\int_V g_{23}\nabla_1 f_{13}\,dr_3 - \frac{1}{v}\int_V (g_{12} + g_{13} + g_{23}) f_{23}\nabla_1 f_{13}\,dr_3, \quad (12)$$

where

$$\Psi_{12} = \frac{1}{v}\int_V f_{23}\nabla_1 f_{13}\,dr_3$$

is a known function.

Equations (11) and (12), together with the con-

dition at infinity (6), constitute a closed system for the determination of the binary correlative function g_{12}, and the physical premises under which this system has been derived correspond exactly to the premises used by Kirkwood to derive the superposition equation [2,4]. Therefore the degree of approximation with which (11) and (12) enable us to obtain g_{12} is very close to that with which g_{12} is obtained from the superposition equation [1]. At the same time, (11) and (12) are linear equations and consequently much easier to solve than the nonlinear superposition equation.

5. We denote by $\psi^{(k)}(r)$ the eigenfunctions of the homogeneous linear equation (11). Then the general solution of (11) can be represented in the form

$$g_{12} = \sum_k A_k g_{12}^{(k)}, \quad g_{12}^{(k)} = \psi_{12}^{(k)}/r_{12}. \tag{13}$$

The constants A_k in (13) can be determined from (12). Indeed, substituting (13) in the latter, we obtain

$$\Psi_{12} = -\sum_k A_k \tilde{g}_{12}^{(k)},$$

$$\tilde{g}_{12}^{(k)} = \nabla_1 g_{12}^{(k)} - \frac{1}{v}\int_V g_{23}^{(k)} \nabla_1 f_{13}\, dr_3$$

$$- \frac{1}{v}\int_V (g_{12}^{(k)} + g_{13}^{(k)} + g_{23}^{(k)}) f_{23} \nabla_1 f_{13}\, dr_3 \tag{14}$$

($0 \le r_{12} \le 2R_0$). This expression is actually an expansion of Ψ_{12} in a system of linearly independent but not orthonormal functions $g_{12}^{(k)}$ in the interval $(0, 2R_0)$. Obviously, such an expansion is possible only when (11) has an infinite number of eigenfunctions.

The boundary condition (14) is equivalent to an infinite system of algebraic equations for the infinite sequence of coefficients [2] A_k. The solution of such a system is, in general, quite complicated. However, as will be shown below, in many cases the series in (13) converges very rapidly. We can then take with sufficient degree of accuracy the m first terms of the series in lieu of (13). The necessary number of algebraic equations for the determination of the m coefficients A_k can then be obtained from (14) by stipulating, for example, that this equation be satisfied identically at m points. We note that this is precisely the procedure used by Kirkwood in the analogous case [5].

6. The equations obtained above enable us to explain the behavior of the binary correlative function at small and large distances. Letting r approach 0 in (11), we obtain

$$g_{12}^{(k)} \to \frac{4\pi}{v}\int_0^\infty \psi^{(k)}(t) f(t)\, t\, dt = \text{const}. \tag{15}$$

It follows directly that the functions $\tilde{g}_{12}^{(k)}$ are finite as $r \to 0$. And since $\Psi_{12}(0) = \text{const} < \infty$, it is obvious that the g_{12} determined with the aid of (13) also remains bounded as $r_{12} \to 0$.

Let us consider now the region of large r_{12}. If r_{12} is so large that the condition $r_{12} \to 2R_0$ is satisfied, then Eq. (11) according to (7) assumes the form

$$\psi(r) = \frac{2\pi}{v}\int_0^{R_0} [\psi(r-\lambda) + \psi(r+\lambda)]\, d\lambda \times \int_\lambda^{R_0} f(\tau)\, \tau\, d\tau, \quad 2R_0 \leqslant r \leqslant \infty.$$

Substituting here $\psi = \exp(-\alpha r)$, we readily verify that if α is the root of the transcendental equation

$$1 = \frac{4\pi}{v}\int_0^{R_0} \operatorname{ch} \alpha\lambda\, d\lambda \int_\lambda^{R_0} f(\tau)\, \tau\, d\tau, \tag{16}*$$

then

$$g_{12} = \sum_{k=1}^{\infty} A_k \frac{e^{-w_k x}}{x}, \quad w_k = \alpha_k R_0, \quad x = \frac{r_{12}}{R_0} \tag{17}$$

is the general solution of (11) for $2R_0 \le r_{12} \le \infty$.

Equation (16), like any other transcendental equation, has an infinite number of roots. Therefore the number of eigenfunctions of (11), as expected, is infinite. Since α is contained in (16) in even fashion, the same values of β_k and γ_k correspond to a total of four roots, $\alpha_k = \pm\beta_k \pm i\gamma_k$. However, the terms with $\alpha_k = -\beta_k \pm i\gamma_k$ must be discarded in (17) because they lead to an expression that diverges at infinity.

Thus g_{12} always decreases exponentially at large distances. Further, if there are only repulsive forces between the particles (that is, $f_{12} \le 0$), then (16) has only complex-conjugate roots and consequently $g_{12} \sim r_{12}^{-1}\exp(-\beta r_{12})\cos(\gamma r_{12} + \gamma_0)$; on the other hand, if the forces between particles

[1] Thus, for example, in the case of a rarefied gas, when (11) can be solved by expansion in the small parameter $1/v$, it turns out that Eqs. (11) and (12), like the superposition equation, yield the correct value of g_{12} up to terms of order $1/v$ inclusive. In the case of concentrated systems such a comparison cannot be made in general. It will be shown below, however, that here, too, there is very good agreement between the solution of both equations.

[2] This can be readily verified, for example, by multiplying the left and right halves of (14) by $\exp(im\pi r_{12}/R_0)$, where $m = 0, 1, \ldots$, and integrating the resultant equations with respect to r_{12} from 0 to $2R_0$.

*ch = cosh.

are mainly attractive (for example, in a sufficiently rarefied real gas), then it turns out that (16) has at least two real roots with values smaller than the real parts of the remaining complex-conjugate roots. In this case we have for sufficiently large r_{12}, $g_{12} \sim \exp(-\beta r_{12})/r_{12}$. This agrees qualitatively with the result obtained by numerical solution of the superposition equation [2,4].

7. Let us consider by way of an example a system of rigid spheres, for which

$$f_{12} = \begin{cases} -1, & 0 \leqslant r_{12} < r_0 \\ 0, & r_0 < r_{12} \leqslant \infty \end{cases}$$

In this case (16) assumes the form

$$\nu = -24w^{-2} \operatorname{ch} w \{1 - w^{-1} \operatorname{th} w\}, \quad \nu = v/v_0, \quad v_0 = \pi r_0^3/6,$$
$$w = \alpha r_0 = \lambda \pm i\omega, \tag{18}*$$

while (17) assumes the form

$$1 \leqslant x \leqslant \infty,$$
$$g_{12} = 2 \sum_{k=1}^{\infty} \frac{e^{-\lambda_k (x-1)}}{x} \{B_k \cos \omega_k (x-1) + C_k \sin \omega_k (x-1)\}, \tag{19}$$

since there are no real roots in (18).

The coefficients B_k and C_k in (19) can be determined from the condition (14), which yields after substitution of the corresponding values

$$1 \leqslant x \leqslant 2,$$
$$x^2 (1 - 0.25 x^2) = \sum_{k=1}^{\infty} A_k \Big\{ 2 (w_k + 1)(w_k x + 1) \frac{e^{w_k x}}{w_k^3} + \frac{1}{w_k^3} [w_k^2 x^2 - 2 (1 + w_k)] + \frac{\nu}{6} (1 + w_k x) e^{w_k (1-x)} - x (1 - 0.25 x^2)(x + e^{w_k (1-x)}) \Big\}, \tag{20}$$

where $A_k = B_k + iC_k$ and $w_k = \lambda_k + i\omega_k$ for $k = 2m$, and $A_k = B_k - iC_k$ and $w_k = \lambda_k - i\omega_k$ for $k = 2m + 1$. In this case the region $0 \leq x < 1$ can be disregarded, since it makes no contribution whatever to $G_{12} = \gamma_{12}(1 + g_{12})$, because $\gamma_{12} \equiv 0$ when $0 \leq x < 1$.

In order to determine the character of the variation of g_{12} with the relative volume ν per molecule, it is necessary to investigate the behavior of the roots of (18). Going over from one equation for $w = \lambda \pm i\omega$ to two equations for λ and ω, we get

$$\frac{\operatorname{th} \lambda}{\lambda} = \frac{\lambda^2 (2\omega + \operatorname{tg} \omega) + \omega^2 (2\omega - 3 \operatorname{tg} \omega)}{\lambda^4 \operatorname{tg} \omega + 3\lambda^2 \omega - \omega^3 (1 + \omega \operatorname{tg} \omega)},$$
$$\nu = \frac{24 \operatorname{ch} \lambda}{\lambda^2 + \omega^2} \Big\{ \frac{\omega^2 - \lambda^2}{\lambda^2 + \omega^2} \cos \omega - \frac{2\lambda\omega}{\lambda^2 + \omega^2} \operatorname{th} \lambda \sin \omega + \lambda \frac{\lambda^2 - 3\omega^2}{(\lambda^2 + \omega^2)^2} \times \operatorname{th} \lambda \cos \omega + \omega \frac{3\lambda^2 - \omega^2}{(\lambda^2 + \omega^2)^2} \sin \omega \Big\}. \tag{21}†$$

*th = tanh.

†tg = tan.

This system is best investigated by specifying the value of ω. We can then obtain from the first equation of (21) the value of λ corresponding to the given ω, and from the second equation the corresponding value of ν.

The first equation of (21) has real roots only when ω satisfies the condition

$$k\pi \leqslant \omega_k \leqslant \omega_k^* = k\pi + \Omega_k^*,$$
$$\operatorname{tg} \Omega_k^* = \frac{3 (k\pi + \Omega_k^*)}{3 - (k\pi + \Omega_k^*)^2}, \quad k = 1, 2, \ldots, \tag{22}$$

with negative values of ν corresponding to all even values of k, and positive values corresponding to the odd k. When ω increases from $k\pi$ to $k\pi + \Omega_k^*$, the damping decrement λ decreases monotonically from infinity to zero, and $|\nu|$ decreases from infinity to $|\nu_k^*|$, where ν_k^* is defined as

$$\nu_k^* = \frac{24 \cos \omega_k^*}{(\omega_k^*)^2 - 3}, \qquad k = 1, 2, \ldots \tag{23}$$

With increasing number of the root k, we have $\Omega_k^* \to \pi$ and $\nu_k^* \to (-1)^{k+1} 24/\pi^2 (k+1)^2 \to 0$. For $k = 0$ there are two real roots corresponding to the same negative value $\nu < \nu_0^* = -8.9664$. When $\nu = \nu_0^*$ these roots coalesce and vanish.

We note still another characteristic point of (21), namely a point at which the real and imaginary parts of w_k are equal, that is, $\lambda_k^{**} = \omega_k^{**} = k\pi + \Omega_k^{**}$. As follows from (21), the quantities ω_k^{**} and λ_k^{**} are determined by the equations

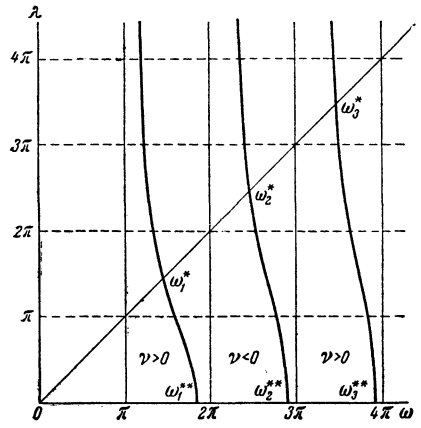
$$\operatorname{tg} \Omega_k^{**} = [2k\pi - \operatorname{th} (k\pi + \Omega_k^*)] + 2\Omega_k^{**} \approx (2k\pi - 1) + 2\Omega_k^{**},$$
$$\nu_k^{**} = -12 (\omega_k^{**})^{-2} \operatorname{ch} \omega_k^{**} \times \{\operatorname{th} \omega_k^{**} [\sin \omega_k^{**} + \cos \omega_k^{**}/\omega_k^{**}] - \cos \omega_k^{**}\} \approx -12 (\omega_k^{**})^{-2} \operatorname{ch} \omega_k^{**} \{\sin \omega_k^{**} + \cos \omega_k^{**}/\omega_k^{**} - \cos \omega_k^{**}\};$$
$$k = 1, 2, \ldots \tag{24}$$

It is easy to see that as $k \to \infty$ we have $\Omega_k^{**} \to \pi/2$ and

$$\nu_k^{**} \to \frac{48 \operatorname{ch} (\pi (2k+1)/2)}{\pi^2 (2k+1)^2} \to \infty.$$

The general character of the variation of $\lambda = \lambda(\omega)$ is shown in the figure, and the values of Ω_k^*, ν_k^*, Ω_k^{**} and ν_k^{**} for k = 1, 2, and 3 are listed in Table I.

We see from the second equation in (21) that the expression in the curly brackets is approximately equal to unity for all λ and ω. Therefore $\nu \approx 24 \cosh \lambda/(\lambda^2 + \omega^2)$. However, since $\omega_k \approx \omega_{k-2} + 2\pi$, the larger the number of the root k, the larger the value of λ_k corresponding to the



same ν = const (since the increase in the denominator, which is proportional to ω^2, can be compensated only by increasing the numerator, which is proportional to cosh λ). Thus, the larger the number of the root, the larger the exponent in (19) and the smaller the contribution made to g(x) by the term corresponding to the given root.

In Table II are listed some specific values of λ_k and ω_k, and also of B_1 and C_1, calculated with the aid of equations obtained after equating at the point x = 1 the values of the functions in the right and left halves of (20) and their derivatives. As can be seen from these data, at all values of the relative volume ν, the quantities B_1 and C_1 are smaller than unity and consequently $G_{12} = \gamma_{12}(1 + g_{12}) \geq 0$. Satisfaction of the last condition is obviously necessary, since G_{12} has the meaning of a probability.

In the last column of Table II are listed the values of pv/Θ, obtained[4] by numerical solution of the Kirkwood superposition equation, while the next to the last column contains the values of the same quantity, calculated by means of the formula[2]

$$pv/\Theta = 1 + 4(v_0/v)[1 + g(1)];$$

$$g(1) = \sum_{k=0}^{\infty} B_{2k+1} \approx B_1 \qquad (25)$$

(the summation in (16) is only over the odd k, since positive ν corresponds only to odd k). It is seen from these data that the agreement between the equations of state obtained by two different methods is fully satisfactory over almost the entire density interval. However, at very high densities ($\nu \lesssim 2$) the superposition equation has in general no solution at all, whereas the solution of (16) exists at all possible $\nu \geq \nu_{min}$, where ν_{min} = 1.35 corresponds to close packing of the spheres. The latter is physically more understandable, for it is difficult to visualize any phase transitions at all in a system of rigid spheres simulating a real gas at a very high temperatures.

It is also of definite interest to compare the form of the function g(x), defined by Eq. (19), with what is obtained by solving the superposition equation. A qualitative correspondence is obvious here, for in both cases g(x) is a periodically damped function[4]. A quantitative comparison, on the other hand, is easiest to carry out by using for the oscillation period a value $T_1 = 2\pi/\omega_1$. It follows from Table II that when ν increases from 1.65 to 5.62, T_1 increases from 1.14 to 1.24, whereas from the data given by Hill[4] it follows that the period increases from 1.18 to 1.26 when ν increases from 2.07 to 6.95—an excellent agreement.

In conclusion the author considers it his pleasant

Table I

k	Ω_k^*	$\omega_k^* = k\pi + \Omega_k^*$	ν_k^*	Ω_k^{**}	$\omega_k^{**} = k\pi + \Omega_k^{**}$	ν_k^{**}
1	150°12′	5.763	0.689	83°01′	4.591	25.20
2	161°06′	9.095	—0.286	86°03′	7.785	—186.8
3	166°04′	12.323	0.156	87°16′	10.948	262.8

Table II

$\nu = v/v_0$	λ_1	λ_3	ω_1	ω_3	B_1	C_1	pv/Θ	$(pv/\Theta)_{sup}$
1.645	1.604	3.11	5.500	11.92	0.260	—0.695	4.064	—
3.223	2.242	3.73	5.300	11.85	0.252	—0.240	2.554	3.7
5.615	2.846	4.32	5.100	11.79	0.165	—0.133	1.830	2.2
9.808	3.473	4.88	4.900	11.71	0.0987	—0.0206	1.448	1.53
17.031	4.121	5.42	4.712	11.62	0.0573	+0.0003	1.248	1.28
25.20	4.591	5.76	4.591	11.57	0.0385	0.0052	1.165	1.17

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