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ITERATIVE SOLUTIONS OF KIRKWOOD'S INTEGRAL FOR LIQUID ARGON

BY

EUGENE D. FABRICIUS

A

THESIS

submitted to the faculty of the
University of Missouri School of Mines and Metallurgy
in partial fulfillment of the work required for the
Degree of
MASTER OF SCIENCE, PHYSICS MAJOR
Rolla, Missouri
1958

Approved by Louis H. Lund
Professor of Physics

ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation for the interest and guidance extended to him throughout the course of this research by Dr. Louis H. Lund, Professor of Physics at the University of Missouri School of Mines and Metallurgy, Rolla, Missouri.

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INTRODUCTION

A liquid or a dense gas may be regarded either as a very imperfect gas in which multiple collisions are frequent or as a distorted crystal in which the long range order has been lost. The crystal-like approach has not led to formal solutions, but it has led to several approximate treatments which can be used to give numerical results.

The two main types of approaches which have been used are: the cell theories, in which the liquid is regarded as a distorted crystal with one molecule located at or near each lattice point; and the hole theories, in which it is realized that liquids differ from crystals in that some of the lattice sites are vacant.

In the cell theory a solid composed of molecules without internal degrees of freedom is pictured as a set of particles executing small vibrations about their equilibrium positions. The partition function of such a system is the product of harmonic oscillator partition functions. In the Einstein approximation each of the molecules is pictured as vibrating independently in that field which would be present if all the neighboring molecules were at their equilibrium positions. To this approximation all the vibration frequencies are the same, and the partition function for a system of N particles is just the product of N identical factors.[1]

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1. R. H. Fowler and E. A. Guggenheim, Statistical Thermodynamics, Cambridge University Press, (1949).

The concept of small vibrations is not valid in liquids. However, since the specific heat of a material in the liquid phase just above the melting point is almost the same as that for the solid phase, it is tempting to retain the idea of the molecule moving in the force field which would exist if all the neighboring molecules were at their mean positions.

There have been two major developments of the cell theories: that of Eyring[2] and his colleagues and that due to Leonard-Jones and Devonshire[3]. Both these groups of investigators established their theories of the liquid state by means of well-founded physical intuition. The basic expressions which were the starting point for their researches have been justified by Kirkwood,[4] who has shown rigorously what assumptions are inherent in both theories. Kirkwood, starting from the general principles of statistical mechanics and using certain well defined approximations, expresses the Gibbs configuration integral as a sum of integrals corresponding to single and multiple occupancy of the cells of a reference lattice. The integral corresponding to single occupancy is then evaluated with the approximate probability density, expressed as a product of functions of the coordinates of individual molecules, which leads to minimum free energy under

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2. H. J. Eyring and O. Hirschfelder, J. Phys. Chem. 41, 250 (1937)

3. J. Lennard-Jones and A. Devonshire, Proc. Roy. Soc. A163, 53 (1937); 165, 1 (1938).

4. J. G. Kirkwood, J. Chem. Phys., 18, 380 (1950).

the restraints of constant temperature and volume. The minimization of the free energy gives an integral equation for the probability density within each cell of the lattice. A first approximation of the solution of this equation yields a partition function identical with that of the Lennard-Jones Devonshire free volume theory. If convergent, an iteration of Kirkwood's integral equation might provide an improvement on the Lennard-Jones Devonshire theory.

The purpose of this research is to determine whether or not the iteration of Kirkwood's integral equation is convergent for liquid Argon.

REVIEW OF LITERATURE

The equations of state of van der Waals[5] and others were successful in accounting for the critical phenomena of gases and the forms of temperature isotherms below the critical temperature. These theories were based on arguments which are valid only for gases of low concentration where binary encounters are predominant, hence they fail for gases at high densities such as obtain near the critical point.

There were also several theories of the crystal state, based on various simple models, the most notable being the Einstein model, and the Debye model.[6] Eyring[7] defined the entropy of fusion as the increase of entropy due to the fact that in the solid state the motion of the individual molecules is restricted to the corresponding individual cells, whereas in the liquid each atom can be found in any cell. This focuses attention on the essential difference between solids and liquids, namely that a solid possesses long range order while a liquid has only short range order. The fundamental factor which determines the amount of disorder in a liquid is the volume, since at the fusion point the liquid differs from the crystal only by its larger volume; this extra volume being denoted as its "free volume".[8]

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[5] R. H. FOWLER and E. A. Guggenheim, op. cit., p.1.

[6] Ibid.

[7] H. J. Eyring, J. Chem. Phys., <u>4</u>, 283 (1936).

[8] J. Frenkel, <u>Kinetic Theory of Liquids</u>, London, Oxford University Press, (1947).

The first attempts to give a description of liquids with the free volume concept were made by Eyring and Hirschfelder.[9] However, they used the free volume theory to correlate the liquid properties with other properties. Leonard-Jones and Devonshire (LJD),[10] on the other hand, used the free volume concept to explain the properties of the liquid state in terms of the intermolecular potentials.

In the LJD theory each molecule is confined to move in a cell around one of the lattice points of a virtual cubic face-centered lattice with a total number of lattice sites equal to the number of molecules, N, the volume per cell being V/N. The field in which each molecule moves in its cell is the molecular field of the surrounding molecules averaged over all directions, and the partition function of the whole assembly can be expressed as a product of the partition functions of the individual molecules. (This excludes multiple encounters, an approximation which is more appropriate the higher the density.) It is further assumed that each molecule moves on the average in the same field and is confined to the same volume. At sufficiently high densities one can neglect the possibility of migration as being an infrequent event compared with the time spent in any given cell.

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9. J. Hirschfelder, D. Stevenson, and H. Eyring, J. Chem. Phys., 5, 896 (1937).

10. J. Leonnard-Jones and A. Devonshire, op. cit., p.2.

Although the LJD cell model gives a reasonable picture of molecular environment at high densities, it becomes increasingly innacurate as the cell size increases.[11] At low densities restriction to cells will prevent collisions occuring and the method gives no second virial coefficient.

An attempt to extend the cell method to low densities was made by Buehler et al.[12] In addition to the model used by LJD which he calls the "soft center model", Buehler considers another model in which the wandering molecule moves in the field of molecules fixed at the centers of neighboring cells and one fixed at the center of the cell in question. This is called the "hard center model". The arithmetic mean of the two free volumes is then used to construct the partition function. This method reduces to that of LJD at high densities and gives the correct second virial coefficient at low densities. No theoretical justification is given for the averaging process.

Although it is known that the communal entropy increases from zero to "k" per molecule as the volume increases to infinity, no satisfactory theory of the point at which it becomes effective has been advanced. Originally it was suggested by Hirschfelder, Stevenson and Eyring[13] that it becomes available at the melting point. This hypothesis has been examined critically by J. A. Pople,[14] who presents an appropriate

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11. J. A. Pople, Phil. Mag. 42, 459 (1951).
12. Buehler, Wentorf, Hirschfelder, and Curtiss, J. Chem. Phys., 19, 61 (1951).
13. J. Hirschfelder et al, op. cit., p.5.
14. J. A. Pople, Phil. Mag. 42, 459 (1951).

method of calculating the comunal entropy of an ensemble of monatomic particles. Pople divides the available volume into cells a la LJD, and the communal free energy is expressed in terms of a set of parameters related to the probability of various multiple occupancies. Application to an assembly of rigid spheres leads to the conclusion that the communal entropy does not become appreciable until the available volume is over five times that of a close-packed assembly. This suggests that, for more accurate potentials, the communal entropy is practically zero in the solid and liquid states.[15]

One of the difficulties of the LJD theory is that it fails to allow for vacant sites in the lattice. It has long been realized that there are many holes in the lattice structure of liquids.[16] Following an idea originally due to Cernuschi and Eyring, the theory of LJD has been generalized by Rowlinson and Curtiss,[17] and others, to include the possibility of empty lattice sites in the liquid state. However, these theories all hinge on linear approximations of the logarithm of the generalized free volume (i.e. that free volume which accounts for neighboring sites which are vacant.), an approximation which does not describe well the dependence of the generalized free volume on the fraction of nearest neighbor

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[15] J. A. Pople, op. cit., p.6.

[16] J. S. Rowlinson, and C. F. Curtiss, J. Chem. Phys., 19, 1519 (1951).

[17] Ibid.

sites which are vacant. These theories show little improvment over the LJD treatment.

The LJD theory involves two types of approximations; those intrinsic to the free volume concept, and those inherent in the calculations of the free volume itself. Buehler, et al,[18] calculated the free volume for non-interacting rigid spheres taking into account the exact geometry imposed by the face-centered cubic packing. The size and shape are quite different from that of the inscribed spheres which correspond to the LJD approximation. At high densities the equation of state obtained from the exact treatment agrees well with the LJD equation. When the specific volume is greater than twice the cube of the collision diameters, the molecules are no longer confined to cages formed by neighboring molecules. At these low densities the free volume concept is ambiguous. The equation of state depends upon the shape and orientation of the cells with respect to the lattice positions of the molecules. A particular choice which leads to an equation of state that at low densities is accurate through the second virial coefficient is given by a dodecahedron formed by planes bisecting the distances from the neighboring molecules to the origin. There are other shapes and orientations of the cells which would lead to other equations of state having this same property.

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18. Buehler, Wentorf, Hirschfelder, and Curtiss, op. cit., p.6.

One of the limitations of the LJD theory as pointed out by Kirkwood[19] is that a free volume is defined in terms of the Gibbs phase integral, and the free volume is then calculated from purely geometrical models without reference to the Gibbs theory. Kirkwood begins with the general principles of statistical mechanics, and presents a rigerous theory of the free volume, and then shows that the LJD theory represents the first approximation to a general equation. Kirkwood developes a formal expression for the communal entropy term which must be added to the LJD result to allow for the fact that the molecules are not entirely confined to their respective cells. This expression is quite intractable and the communal entropy problem remains unsolved. If the communal entropy is neglected, the problem reduces to one of single occupancy. Considering this case further, Kirkwood seeks the "best" solution, (that is, the one that minimizes the free energy), based on a self-consistant field approximation. The essential feature of this approximation is that a molecule is considered to move not in the instantaneous field produced by its neighbors, but in the average field produced by its neighbors as they move over their cells. The self-consistant feature of the calculation enters through the necessity of finding a potential probability distribution function which yields an averaged LJD cell potential that then reproduces, through the Boltzman factor, the original

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[19] J. G. Kirkwood, op.cit., p.2.

probability function. Kirkwood obtains an integral equation which is equivalent to this condition. Although Kirkwood's equations formally determine the best solution of the restricted class of solutions he considers, the accuracy of the self-consistant field approximation is open to question. The true situation is that each molecule moves in the instantaneous field of its neighbors and not in an average or smeared-out field.

Taylor[20] attempts to take account of this fact by assuming that the configurational probability function for the entire liquid is a product of separate functions, one for each molecule. Thus Taylor recasts the exact classical partition function in a form in which the LJD potentials appear in correction terms. The resulting integrals are analogous to those appearing in the conventional theory of an imperfect gas, but with the correlation potential playing the role of the usual intermolecular potential, and the range of integration of each molecule limited to its own cell, where it is also subject to the static LJD potential. A practical method of evaluation of the integrals is developed, based on power series expansions of the factors containing the correlation potentials. Single occupancy is not an essential feature of this theory, and the allowance for multiple occupancy leads to the communal entropy correction.

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[20] W. J. Taylor, J. Chem. Phys., 24, 454 (1956).

DeBoer[21] generalizes the LJD theory by considering in a systematic way the motion of two or more neighboring molecules in a "cell-cluster" of two or more neighboring cells, considered as one big cell shared collectively by the molecules in the cell-cluster. This method solves in principle the problem of communal entropy and problems related to the correlation of the motions, and allows for quantum mechanical treatment of exchanges of neighboring molecules. On the basis of this concept of the cell-clusters deBoer is able to define a set of partial probabilities for n molecules in a cell-cluster of n cells. This set of probabilities has as its first number the single cell probability of LJD, and as its last number the true probability which should be introduced into the partition function. The calculation of the partition function of the cell-cluster method leads to the difficult combinatorial problem of finding the factor for the number of ways of distributing a given number of cell-clusters of given size and shape over the lattice, and in general an exact solution is difficult to obtain.

Wood[22] gives an exact solution to the Kirkwood integral for a system composed of rigid spheres by considering the face-centered cubic lattice and choosing as the cell the dodecahedrȯn proposed by Buehler et al. Wood's solution gives zero for the integral if the molecule is in the dodecahedron, and infinity elsewhere.

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21. J. deBoer, Physica <u>20</u>, 655 (1954).

22. W. W. Wood, J. Chem. Phys., <u>20</u>, 1334 (1952).

Lund[23] shows that apparently Wood's solution will hold for other types of molecular packing where the potential within the cell is uniform and is effectively infinite at the boundary, and where the free volume is defined to be: $(v^{1/3} - r_0)^3$ times the lattice parameter, a.

The LJD theory has proved to be an effective method of treatment of liquids and dense gases, because of its simplicity and the fact that it predicts the essential features of the condensation process on the basis of the intermolecular potential, and from the practical viewpoint provides the best estimates of PVT properties for gases and liquids at very high pressures and temperatures.

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[23] L. H. Lund, J. Chem. Phys., 20, 1977 (1952)

THEORY

In the LJD model of the liquid, the molecule whose partition function is to be determined is considered to be moving in its neighborhood under the potential interaction of its neighbors, which are assumed to be fixed at their equilibrium positions. The volume allowed it by its neighbors is defined as the free volume of the molecule. For mathematical expediency in computing the potential due to the neighboring molecules, LJD considered the nearest neighboring molecules to be uniformly distributed over a spherical surface, and neglected the effect of all other molecules. Kirkwood, beginning with the general principles of statistical mechanics, presents a rigerous theory of the free volume, thus putting the LJD theory on a firm foundation.[24]

Let v = Volume of the system.
T = Absolute temperature of the system.
k = Boltzman's constant.
h = Plank's constant.
V_n = Potential of intermolecular force.
Δ_j = Volume of cell j.
A_n = Free energy of the system.
Z_n = Gibbs phase integral in configuration space.
N = Number of monatomic molecules in volume v.
m_j = Number of molecules in cell j.

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[24] J. G. Kirkwood, op. cit., p.2.

$\vec{r}_j$ = Position vector of jth particle referred to an origin in cell j.

$\vec{R}_{ik}$ = Vector from origin of cell i to origin of cell k.

The classical expression for the partition function of an assembly of N monatomic molecules is:

(1) $(2\pi mkT/h^2)^{\frac{3N}{2}} \; Z_n/N!$,

(2) $Z_n = \int^{v}\cdots\int^{v} e^{-\beta V_n}\prod_k dv_k$, where $\beta = 1/kT$,

(3) $V_n = \sum_{i=k=1}^{N} V(\vec{R}_{ik})$.

If the volume v is spanned by a virtual lattice of N cells, Δ_j, each of volume Δ, the integral over v in the configuration space of each molecule may be expressed as a sum of integrals over the individual cells:

(4) $Z_n = \sum_{k_1=1}^{N}\cdots\sum_{k_N=1}^{N}\int^{\Delta k_1}\cdots\int^{\Delta k_N} e^{-\beta V_N}\prod_k dv_k$.

The choice of lattice is arbitrary, and will be chosen for convenience such that the number of cells is equal to the number of molecules N. The N^N integrals of equation (4) may all be expressed in terms of integrals of the type $Z_n^{(m_1\cdots m_n)}$, where:

(5) $Z_n^{(m_1\cdots m_n)} = \int^{\Delta k_1}\cdots\int^{\Delta k_N} e^{-\beta V_N}\prod_k dv_k$.

Therefore, equation (4) becomes:

(6) $Z_n = N!\sum_{m=1}^{N} Z_n^{(m_1\cdots m_n)}/\prod m_s!$.

Now, the integral corresponding to single occupancy of each cell is:

$$(7) \quad Z^{(1\ldots1)} = Z^{(1)} = \int^{\Delta_1}\cdots\int^{\Delta_N} e^{-\beta V_N} \prod_k dv_k,$$

and:

$$(8) \quad Z_n = N! \; \sigma^N Z^{(1)},$$

where:

$$(9) \quad \sigma^N = \sum_{m_1,\ldots,m_N=0}^{N} \frac{1}{m_s!} \, Z^{(m_1\ldots m_n)}/Z^{(1)}.$$

Sigma takes into account the "cooperative" motion and contributes the "communal entropy". It is easily shown that sigma equals one at high density, and e at low density. This arbitrary use of sigma equals e was assumed by Eyring in his work and leads to his definition of communal entropy.

The phase integral $Z_n^{(1)}$ is related to the relative probability density in configuration space $P_n^{(1)}$ subject to single occupancy by:

$$(10) \quad P_n^{(1)} = \exp\beta\,(A_n^{(1)} - V_n).$$

With a little manipulation it can be shown that the equation of total free energy is given by:

$$(11) \quad A_n = -NkT \ln \left[(2\pi mkT/h^2)^{3/2}\sigma\right] + A_n^{(1)}.$$

Using an approximation similar to that employed by Hartree in the solution of the Schrodinger equation for several particles:

$$(12) \quad P_n^{(1)} = \prod_{s=1}^{N} \varphi(\vec{r}_s), \qquad \text{where} \quad \int^{\Delta} \varphi(\vec{r})\, dv = 1.$$

$\varphi(\vec{r}_s)$ depends only on the position of molecule s in cell s referred to some convenient origin in that cell. In this approximation the free energy per mole becomes:

$$(13)\quad A_n/RT = \int^{\Delta}\varphi(\vec{r})\ln\varphi(\vec{r})dv + 1/2kT\iint^{\Delta\Delta'}E(\vec{r}-\vec{r}\,')\varphi(\vec{r})\varphi(\vec{r}\,')dvdv',$$

where: $E(\vec{r}) = \sum_{j}^{N} V(\vec{R}_{1j} + \vec{r})$.

$V(\vec{R}_{1j} + \vec{r})$ is the potential of intermolecular force for a pair of molecules, $\vec{R}_{1j}$ being a lattice vector joining the origins of cell one and cell j. The choice of $\varphi(\vec{r}_s)$ leading to the best approximation to the free energy under the given restraints is that which minimizes $A_n^{(1)}$ at constant temperature and volume. By the method of Lagrange Multipliers one obtains from equation (13) the following integral equation which determines the best approximation to $P_n^{(1)}$ in the form of a product of functions of the coordinates of individual molecules.

$$(14)\quad \psi(\vec{r}) = \int^{\Delta} w(\vec{r} - \vec{r}\,') \exp\beta(\alpha - \psi(\vec{r}\,'))\, dv';$$

$$\text{where:}\quad \exp(-\beta\alpha) = \int^{\Delta}\exp(-\beta\psi(\vec{r}))\, dv,$$

$$\varphi = \exp\beta(\alpha - \psi),$$

$$w(\vec{r}) = E(\vec{r}) - \bar{E},$$

$$\bar{E} = \iint^{\Delta\Delta'} E(\vec{r} - \vec{r}\,')\varphi(\vec{r})\varphi(\vec{r}\,')dvdv'.$$

If $\varphi(\vec{r})$ is sharply peaked in the vicinity of the cell origin, it may be replaced by a Dirac Delta Function in zero approximation. Equation (14) then leads to a first approximation:

$$(15)\quad \Psi_1(\vec{r}) = w_o(\vec{r}),$$

$$\bar{E} = \sum V(\vec{R}_{1j}),$$

$$w_o(\vec{r}) = \sum \left[V(\vec{R}_{1j} + \vec{r}) - V(\vec{R}_{1j}) \right].$$

If the sums defining E_o and $w_o(\vec{r})$ are extended only over nearest neighbor sites, and the nearest neighbor sum is replaced by an integral over a sphere of radius equal to the distance between neighbors, $w_o(\vec{r})$ becomes identical with the LJD theory. If convergent, a numerical solution of the integral (14) may be obtained by iteration, leading to a refinement of the LJD theory.

APPLICATION OF THEORY

For spherical non-polar molecules it has been shown that the energy of interaction between a pair of molecules can be represented satisfactorily by the Lennard-Jones (6-12) type potential, which does not offer the recalcitration to numerical calculations inherent in the Buckingham type potential.[25] The Lennard-Jones potential can be expressed in the form:

$$(16) \qquad \varphi(\vec{r}) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right],$$

where σ is the rigid sphere diameter, (i.e. the distance of closest approach of two molecules which collide with zero initial relative kinetic energy.), and ϵ is the maximum energy of attraction of the two molecules, which occurs at a separation of $r = 2^{1/6}\sigma$.

The parameters σ and ϵ may be used to define the following reduced variables:[26]

$T^* = kT/\epsilon$ = reduced temperature,
$v^* = v/\sigma^3$ = reduced cell volume.

The parametric values used are listed in Table I. Additional simplification of the formulae results from defining the following dimensionless quantities:

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[25] J. Lennard-Jones and A. Devonshire, op. cit. p.2.

[26] J. Hirschfelder, C. Curtiss, and R. Bird, Molecular Theory of Gases and Liquids, New York, Wiley, (1954)

$$y = (\vec{r}/a)^2,$$

$$Y = \left(\frac{\vec{r} - \vec{r}\,'}{a}\right)^2 = (\sqrt{y} - \sqrt{y'})^2;$$

$$l(y) = (1 + 12y + 25.2y^2 + 12y^3 + y^4)(1 - y)^{-10} - 1,$$

$$m(y) = (1 + y)(1 - y)^{-4} - 1\,.$$

Assuming that the wanderer interacts with no molecules farther removed than the shell of nearest neighbors, and replacing the nearest neighbor sum by an integral over a sphere of radius equal to the distance between neighbors, the Lennard-Jones potential $w_o(\vec{r})$ defined in equation (15) becomes:

$$(17)\quad w_o(\vec{r}) = c\epsilon\left[l(y)/v^{*4} - 2m(y)/v^{*2} \right],$$

where c is the number of nearest neighbors; (c = 12 for Argon).

In the Kirkwood derivation of equation (14) the function $w(|\vec{r} - \vec{r}\,'|)$ represents the pairwise interaction force between two molecules as indicated in Figura Ia. It is easily seen that for $\vec{r}\,' = 0$ this reduces to the original Lennard-Jones value. To evaluate $|\vec{r} - \vec{r}\,'|$ it is easier to use figure Ib, from which it is seen that:

$$(18)\quad |\vec{r} - \vec{r}\,'| = (r^2 + r'^2 + 2rr'\cos\omega)^{1/2},$$

where ω is the angle between $\vec{r}$ and $\vec{r}\,'$. Thus, from equation (14):

$$(19)\quad \Psi_2(\vec{r}) = w_1(\vec{r}) = \int^{\wedge} w_o(|\vec{r} - \vec{r}\,'|)\exp\beta\left[\mu - w_o(\vec{r}\,')\right]dv;$$

Where $dv' = 2\pi r'^2 \sin\omega\, d\omega\, dr'$.

Also, from equation (14):

$$(20)\quad \exp[-\beta\alpha_0] = \int_0^{r_0} \exp[-\beta\, w_0(\vec{r})]\, 4\pi r^2 dr,$$

$$= 2\pi a^3 \int_0^{y_0} \exp[-\beta\, w_0(y)]\sqrt{y}\, dy.$$

Defining: $g = \int_0^{y_0} \sqrt{y}\, \exp[-\beta\, w_0(y)]\, dy$, equation (20) may be written:

$$(21)\quad \exp[\beta\alpha_0] = 1/(2\pi a^3 g).$$

Therefore, equation (19) may be expressed in the form:

$$(22)\quad w_1(y) = 12\epsilon/2g \int_0^{\pi}\int_0^{y_0} w_0(Y)\, \exp[-\beta\, w_0(y')]\, \sqrt{y'}\, \sin\omega\, d\omega\, dy';$$

which for the purposes of numerical calculation may be written in the form:

$$(23)\quad w_1(y) = 12\epsilon\, \Delta\omega\, \Delta y'/2g \sum_{\omega}\sum_{y'} w_0(Y)\exp[-\beta\, w_0(y')]\sqrt{y'}\, \sin\omega,$$

where now: $g = \Delta y' \sum_{y'} \sqrt{y}\, \exp[-\beta\, w_0(y)]$.

Finally, when y is zero, equation (23) may be integrated over the angle ω, and the following pair of equations result:

$$(24)\quad w_1(y)/12\epsilon = \Delta\omega\Delta y'/2g \sum_{\omega,y'} w_0(Y)\exp[-\beta\, w_0(y')]\sqrt{y'}\, \sin\omega, \quad y > 0.$$

$$(25)\quad w_1(y)/12\epsilon = \Delta y'/g' \sum_{y'} w_0(y')\, \exp[-\beta\, w_0(y')]\sqrt{y'}, \quad y = 0.$$

In the above summations, the range of summation was taken to be a cell whose volume is equal to the specific volume of the liquid. Thus, the upper limit is given by $y_0 = (3/4\pi\sqrt{2}) = 0.30544$ for a face-centered cubic lattice. The interval was divided into ten values of y, ten values of y', and eighteen values of ω. The order of summation being first over the angle, then over y', for each value of y. The values of g and the summation coefficients used are given in Table II.

Replacing $w_0(y)$ by $w_1(y)$ as calculated by the above method, and repeating the process yields $w_2(y)$, etc. In this manner values of $w_1(y)$, $w_2(y)$, and $w_3(y)$ were calculated with results as shown in Figure II.

For additional accuracy extra care was taken near the origin where the function behaves approximately as the square root of y. The region between y = 0 and y = .03 was subdivided into smaller regions, since it is in this region that the most important values of the function are obtained, the exponent rapidly dying off at larger values of y. The results of this calculation are shown in Figure III.

The rapid rising of the curve for small values of y' as indicated in Figure III causes w(y) to increase in each iteration, finally approaching infinity everywhere.

An investigation of the effect of superposing a **rigid**-sphere potential upon the Lennard-Jones potential was considered. However, as shown in Figure IV, the hard-shell diameter is almost identical to the free volume diameter, and the effect of this superposition is to nullify the Lennard-Jones potential. The results so obtained then become identical with those of Wood.[27]

Only nearest neighbors were considered in the calculations. However, the function was evaluated at three points for three shells of neighbors, using data from the curve for $w_0(y)$. The

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[27] W. W. Wood, op. cit. p.11.

results are in extremely close agreement with the curve for one shell. This is in agreement with results as published by Buehler, et al.[28] Their results show that the inclusion of second and third shells is negligible except at high density.

The summations were performed using the trapezoidal rule. For comparison, graphs of $w_1(y)$ versus ω, and $w_1(y)$ versus y' are given in Figures V, and VI, respectively.

As a check on the computational accuracy the value of g for $w_1(y)$ was compared with values as listed by Buehler et al., and found to be in excellent agreement.[29]

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[28] Buehler, Wentorf, Hirschfelder, and Curtiss, J. Chem. Phys., 18, 1485 (1950).

[29] Ibid.

TABLE I

The values of the parameters used:[30]

σ = 3.45 Angstroms

ϵ = 1.647×10^{-14} Ergs

v = 1.33

T = 0.90

TABLE II

$\Delta\omega$ = 0.1745 Radians

$\Delta y'$ = 0.03

	g	$\Delta\omega\Delta y'/2g$	$\Delta y'/g$
w_1	2.604×10^{-3}	1.005	11.521
w_2	1.520×10^{-5}	344.41	1974

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[30] J. Corner, Trans. Faraday Soc., <u>44</u>, 914 (1948).

FIGURE Ia

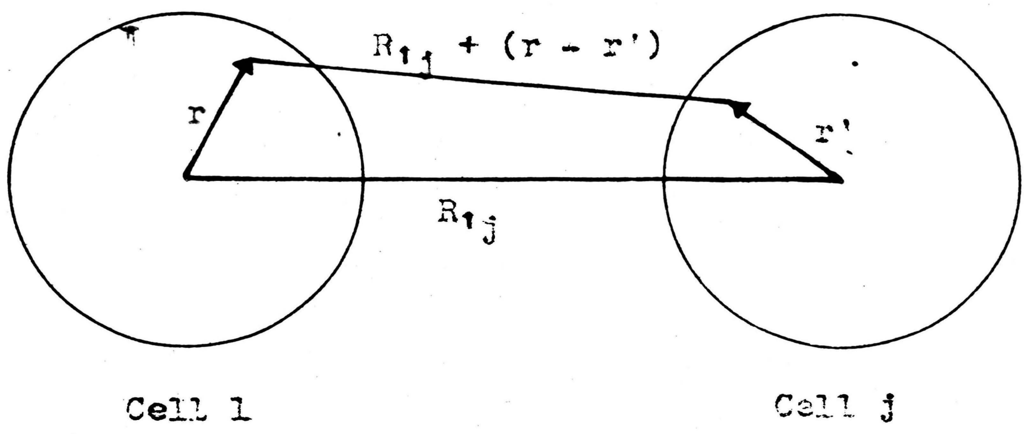

FIGURE Ib

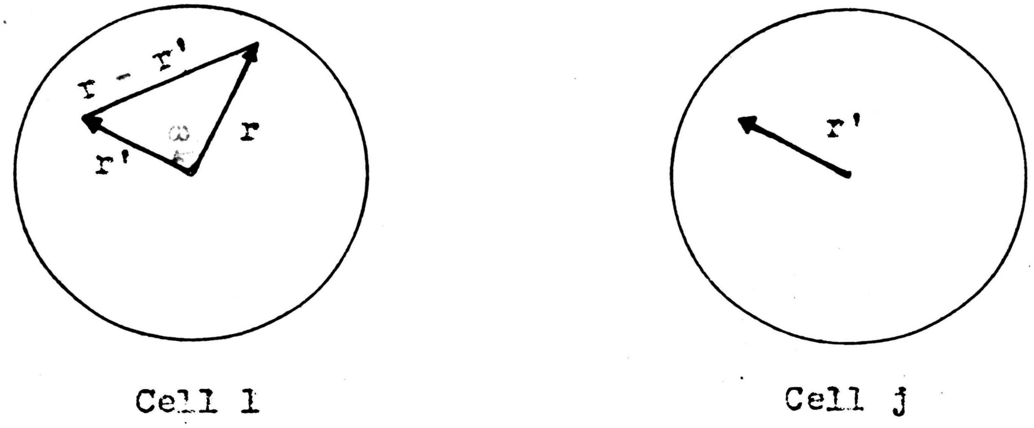

Figure 1: Intermolecular potential diagrams for liquid argon.

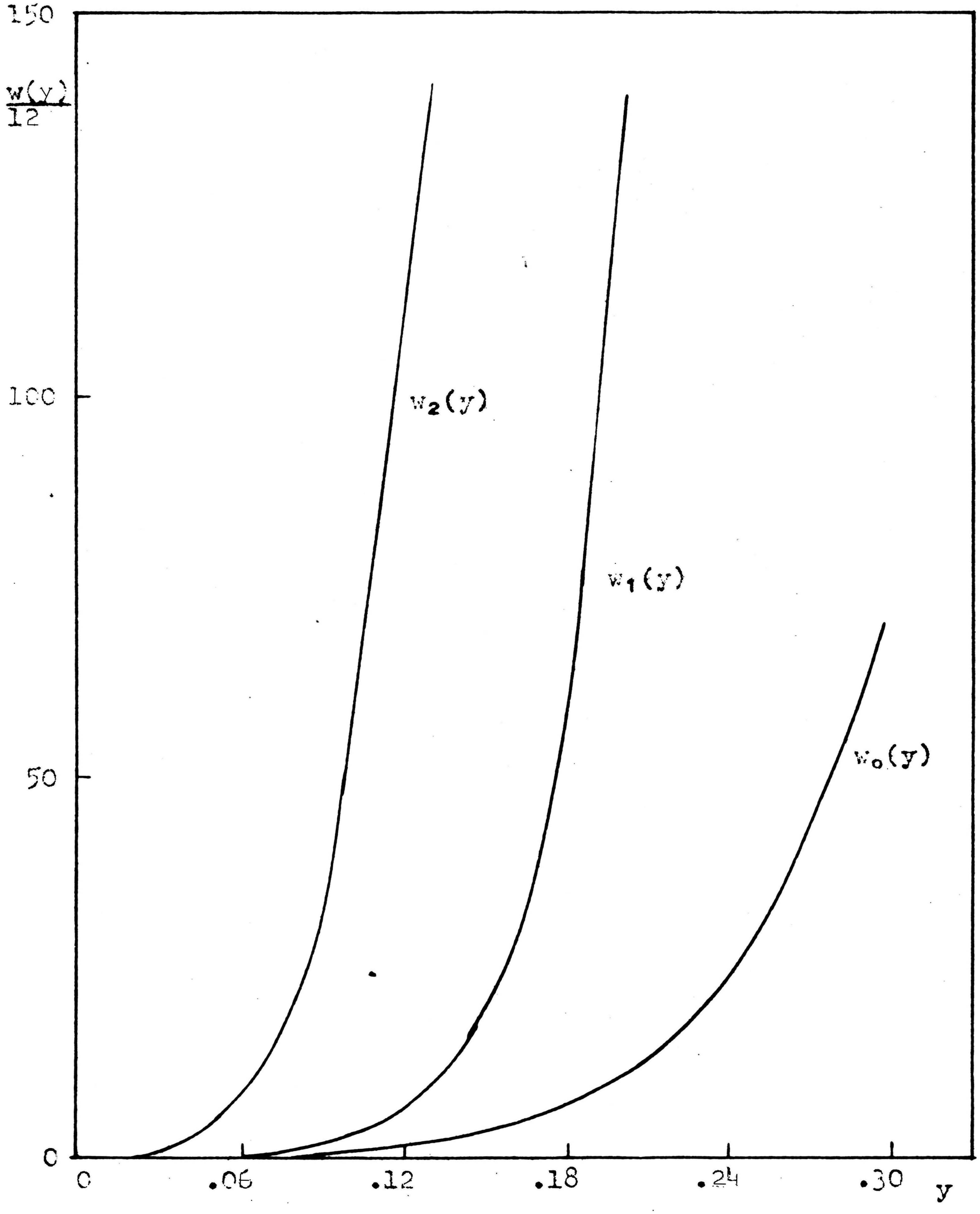

Figure II: w(y) vs. y for free volume cell, initial value, first and second iterations.

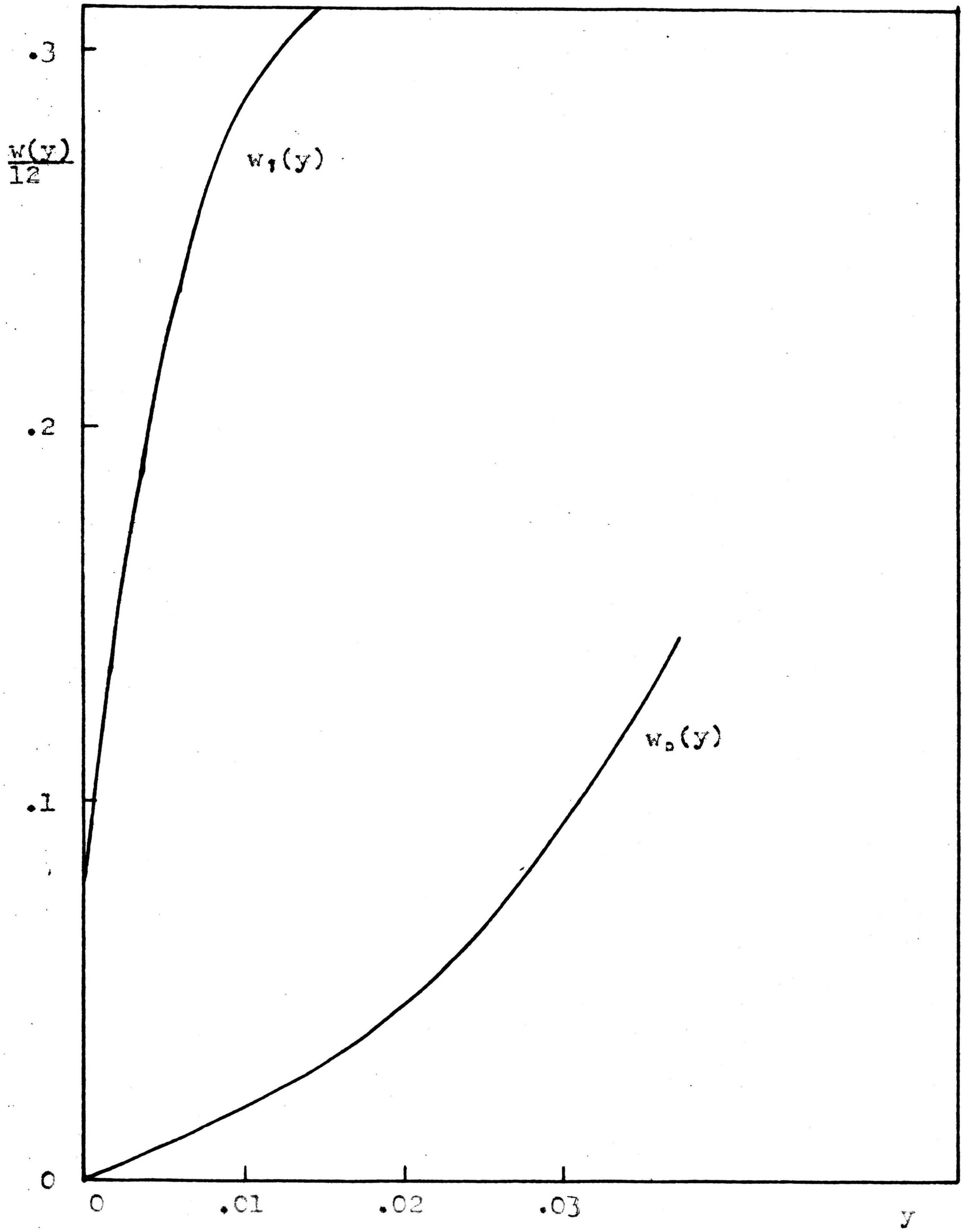

Figure III: w(y) vs. y for small displacements near cell origin.

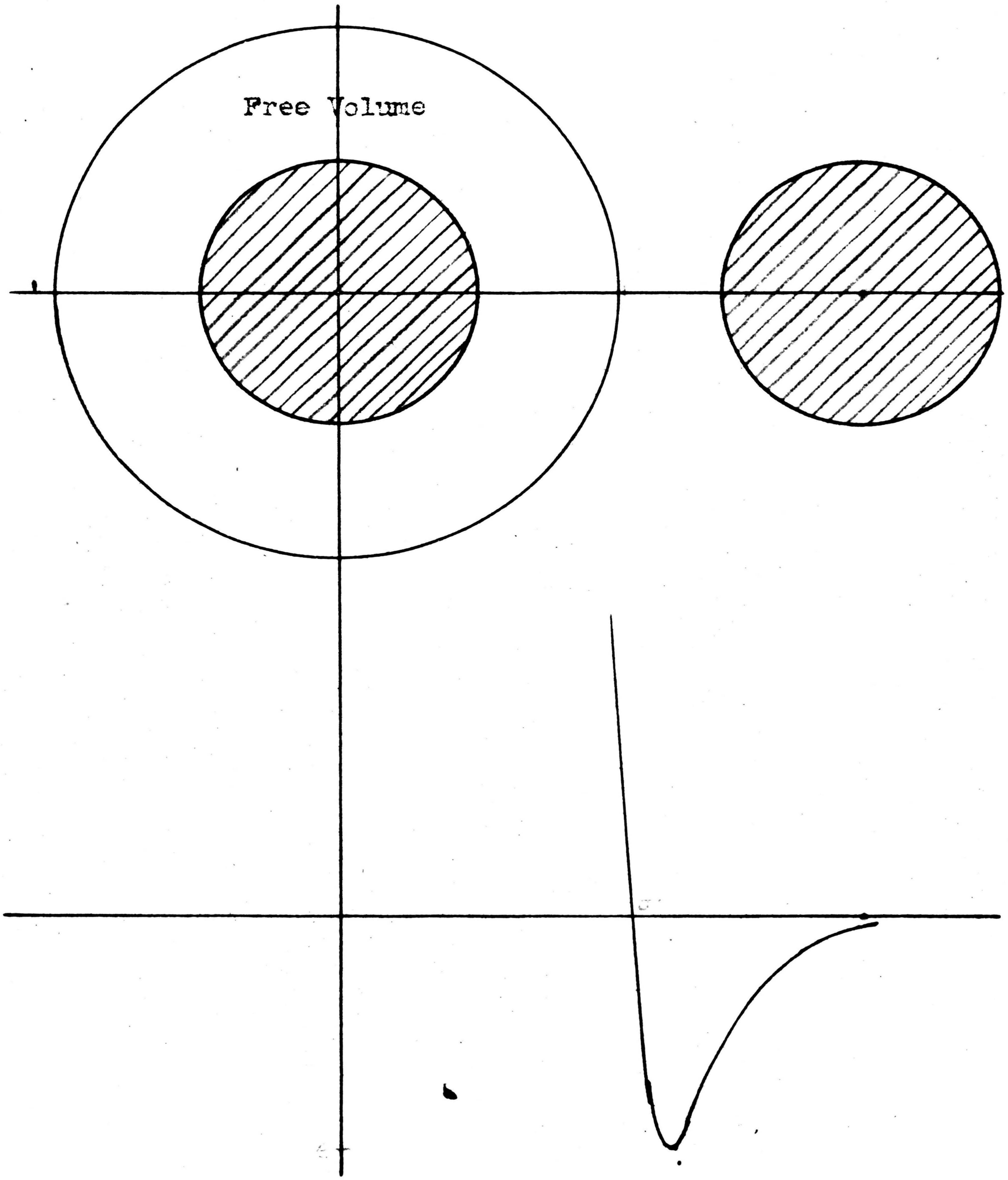

Figure IV: Comparison of collision diameter, free volume cell, and intermolecular potential for argon.

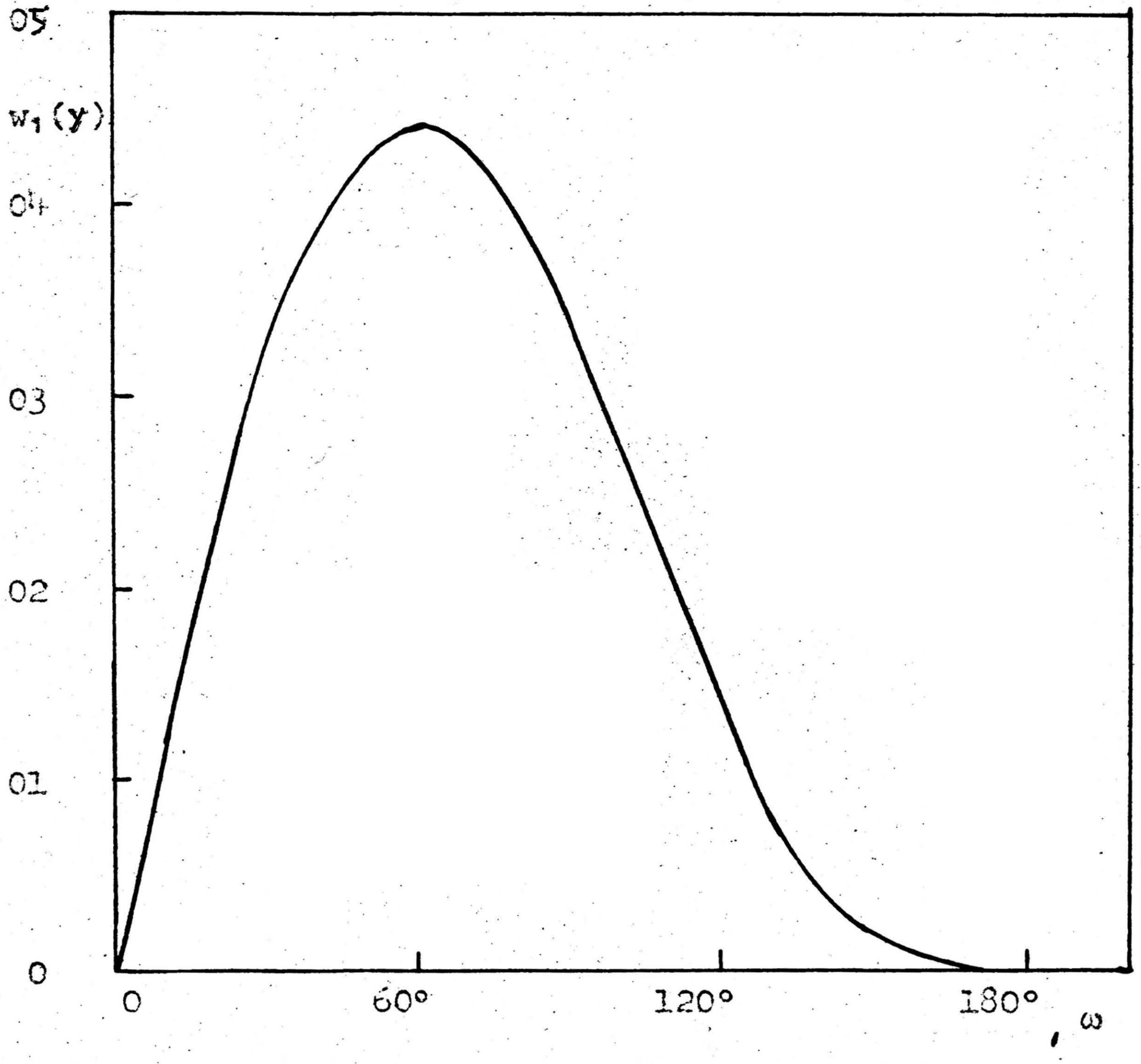

Figure V: $w_1(y)$ as a function of ω for argon; $y = .03$ and $y' = .03$.

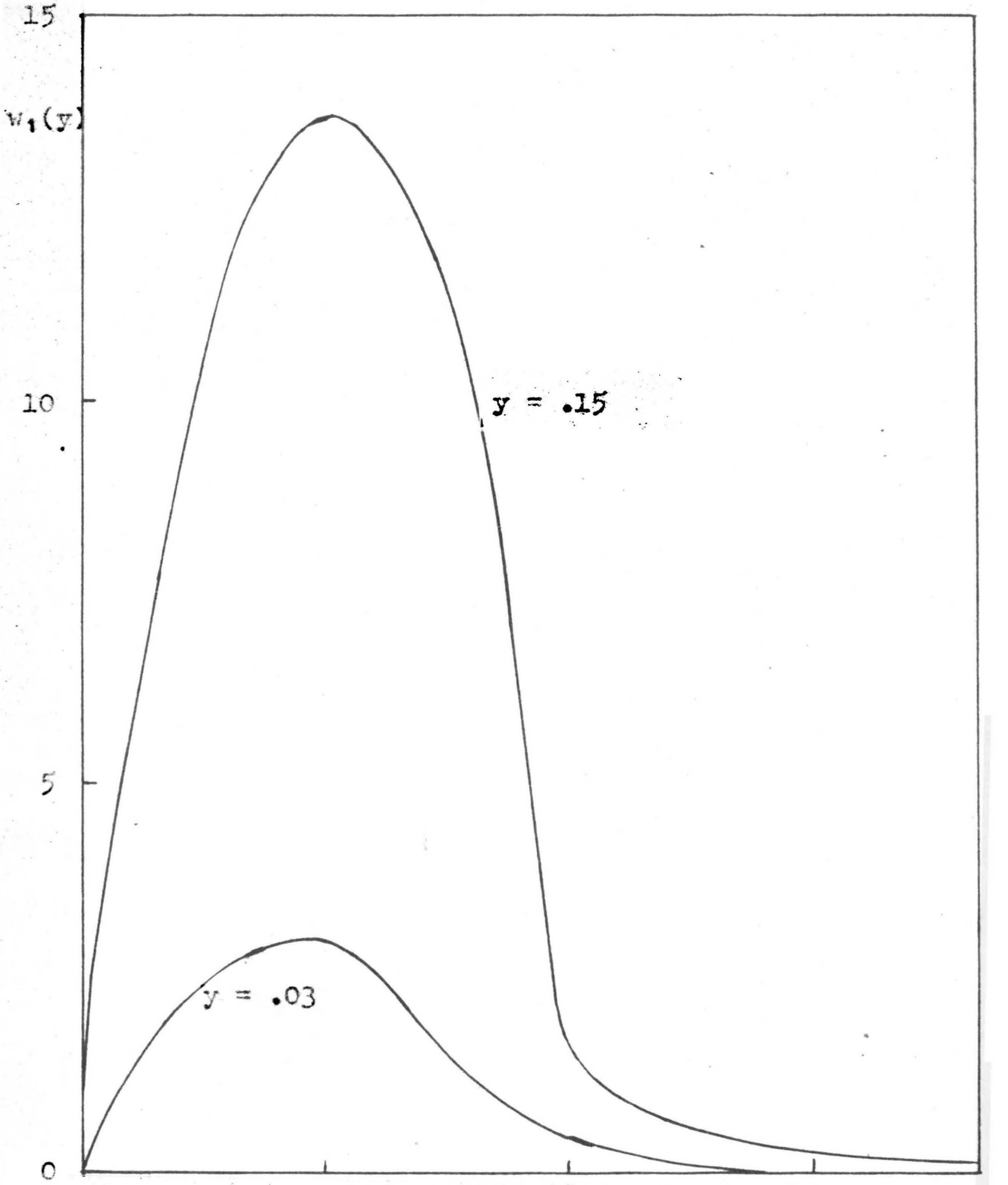

Figure VI: $w_1(y)$ as a function of y' for argon; y = .03, and y = .15.

CONCLUSION

The Kirkwood integral has been iterated and found to diverge for liquid Argon, using the Lennard-Jones type potential, and parametric values as listed in Table I. This divergence appears to be due to the rapid rising of the iterated curve at low values of y where the function varies almost linearly in r. This is in contradiction to accepted theory which states that small displacements from equilibrium give rise to harmonic motion requiring a parabolic potential.

It seems that a correction term added to the Lennard-Jones potential could eliminate this effect. One possibility would be to superpose a rigid sphere potential using a diameter smaller than the actual collision diameter. There is no physical justification for arbitrarily choosing this diameter however, and no way of determining the proper value to choose. One iteration was performed using a collision diameter equal to one-half the actual value with a resultant lowering of the curve of $w_1(y)$ below that of $w_0(y)$. Apparently this value causes the function to approach zero everywhere, although this was not verified. The above results would seem to indicate a suitable value of the collision diameter lying between the true value and one-half the true value.

An alternative approach would be to consider a different cell; perhaps the dodecahedron of Buehler, which appears to be the most appropriate cell from the physical viewpoint. However the calculations become prohibitive for non-spherically symmetric potentials.

SUMMARY

The iteration of the Kirkwood integral was performed using the Lennard-Jones (6-12) potential, for Argon at a temperature of 110°K, with a density of 1.384 gm/cc; two iterations being sufficient to show that the integral diverges.

As a check on the calculations the value of g, equation (23) was compared with the values computed by Buehler, et al, and found to be within the proper range of values.

A probable source of the divergence is given, with several possible methods of eliminating the cause.

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VITA

Eugene D. Fabricius was born December 6, 1929, in DeSoto, Missouri, the son of Charles and Laura Fabricius. He received his elementary education in the parochial schools of Saint Louis, through the first year of high school.

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