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DIRECT CORRELATION FUNCTIONS
FOR LIQUID ARGON

BY

ARTHUR REETZ, JR.

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
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Approved by Louis H. Lund
Professor of Physics

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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

It is possible to predict the intensity of coherently scattered waves by a liquid in thermodynamic equilibrium if the distribution of the atoms or molecules, about one chosen arbitrarily, is known completely. It has been shown in a one-dimensional model that certain distances receive special weight in the formation of interferences.[1] Qualitatively it is possible to determine a spatial distribution function because of the impossibility of interpenetration of atoms and the implication that certain arrangements of any given atom with respect to its neighbors are more probable than others. However, by using the simplest case of atoms as hard spheres, it has not been possible to calculate unambiguously and exactly the distribution of atoms about any given atom; and as yet definite results have not been obtained for a procedure based on first principles because of analytical complications.[2]

In view of this a number of attempts have been made to solve the problem by semi-empirical means. Ornstein and Zernike[3], among others,[4] have derived a quite general semi-empirical liquid model. It was suggested by Zernike and Prins[5]

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1. F. Zernike and J. A. Prins, Z. Physik 41, 184 (1927).

2. J. E. Mayer and M. G. Mayer, Statistical Mechanics, N. Y., Wiley, (1941).

3. L. S. Ornstein and F. Zernike, Proc. Acad. Sci. Amsterdam 17, 793 (1914).

4. J. Frenkel, Theory of Liquids, London, Oxford University Press, (1947).

5. F. Zernike and J. A. Prins, op. cit.

that if the coherent scattering structure factors of x-rays were known precisely, then the reverse of the above procedure is available and the two- atom or two-molecule spatial distribution function, which is one of the two operating elements of the Ornstein-Zernike (O. Z.) model, can be determined. Debye and Menke[6] completed the theoretical work on determining this spatial distribution function and applied it to liquid mercury. An alternate presentation of this theory along with a discussion of the method and application to various liquid elements has been given by Gingrich.[7]

The O. Z. liquid model is based on the assumption that there is a direct intermolecular interaction function whose range is of the same order of magnitude as that of the intermolecular forces. It is this direct interaction function which in turn determines an indirect interaction function which enters into the static two-atom radial distribution function. This two-atom distribution function defines the probability per unit volume of finding an atom at some specified distance r from an origin atom.

The fundamental relation of the O. Z. liquid model is the definition of the indirect interaction function in terms of the direct interaction function. According to Goldstein[8] this relationship has been left partially out of account in

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6. P. Debye and H. Menke, Ergeb. d. Tech. Rontgenk II (1931).
7. N. S. Gingrich, Rev. Mod. Phys. <u>15</u>, 90 (1943).
8. L. Goldstein, Phys. Rev. <u>84</u>, 466 (1951).

x-ray work. Therefore, Goldstein[9] has attempted to redirect attention to the possibility of obtaining a more complete verification of the O. Z. liquid model through a fuller exploitation of the experimental data already accumulated on the coherent intensity factors of a number of liquids.

Further interest in the O. Z. static liquid model has been aroused by a study of the analogies existing between the molecular distributions of this model and that of ideal Bose-Einstein fluids undergoing condensation in momentum space.[10] Additional verification of the O. Z. theory in the critical region of liquids may possibly come about by using slow neutrons in the investigation of the coherent scattering by liquids in this region.[11, 12]

The purpose of this research is to obtain the direct interaction functions from the liquid argon x-ray scattering structure factors of Eisenstein[13] at various temperatures and over a wide range of interatomic separations.

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9. Ibid.

10. L. Goldstein, Phys. Rev. 83, 289 (1951).

11. Ibid.

12. L. Goldstein, Phys. Rev. 81, 326A (1951).

13. A. Eisenstein and N. S. Gingrich, Phys. Rev. 62, 261 (1942).

REVIEW OF LITERATURE

Considerable information concerning the atomic distribution in matter, both crystalline and amorphous, has been obtained from x-ray scattering patterns. Beginning with the advent of reliable experimental techniques for obtaining these x-ray patterns, many attempts have been made to give a quantitative description of the structure of liquids.

In 1914 Ornstein and Zernike[14] suggested a liquid model in connection with a possible solution of the critical opalescance problem of visible radiation. Since that time many advances in both experimental technique and theory of the subject have been made. A relation involving an indirect correlation or distribution function was derived by Zernike and Prins.[15] They specified a distribution function from which x-ray intensities could be calculated and compared with existing experimental data. Debye and Menke,[16] however, used experimental data to determine the nature of the distribution function. It was thus shown that the probability that the atomic or molecular spacing in a liquid has a specific value. G. W. Stewart[17] in numerous articles supported the theory that the atomic or molecular grouping in a liquid is arranged temporarily, and for short spatial distances, in the same

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[14] F. Zernike and J. A. Prins, op. cit., p.1.

[15] L. S. Ornstein and F. Zernike, op. cit., p.1..

[16] P. Debye and H. Menke, op. cit.; P. Debye, Z. Physik 31, 348 (1930).

[17] G. W. Stewart, Rev. Mod. Phys. 2, 116 (1930).

manner as in the solid state. An excellent review of the work on coherent scattering of x-rays by liquid elements has been prepared by Gingrich.[18]

In 1951 Goldstein[19] called attention to the fact that the fundamental relationship of the original Ornstein-Zernike liquid model has been partially omitted in the analysis of x-ray scattering data. This fundamental relation

$$(1) \quad g(\bar{r},T) = \int f(\bar{r}-\bar{r}',T)\, g(\bar{r}',T)\, dv' + f(\bar{r},T),$$

where the integration extends over the liquid volume at temperature T and $\bar{r}$ is a vector from an arbitrary origin atom in the liquid to an atom at r, states that the indirect interaction or correlation between a molecule at the origin and one at a distance r is equal to the direct interaction $f(\bar{r},T)$ with the molecule at r plus the sum of the correlations with those molecules surrounding the one at the origin which are caused by their direct interaction with the molecule at r. This relation has recently been derived by Klein and Tisza[20] in their discontinuous transcription of the Ornstein-Zernike continuum liquid model.

A knowledge of the indirect interaction function g(r,T) enables with some effort the determination of the direct

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[18] N. S. Gingrich, op. cit., p.2.

[19] L. Goldstein, op. cit., p.2.

[20] M. J. Klein and L. Tisza, Phys. Rev. 76, 1861 (1949).

interaction function f(r,T) according to the integral equation (1). Goldstein[21] has derived the direct interaction function in terms of the coherent intensity structure factor of x-rays by means of a Fourier inversion. This derivation allows the same type of numerical analysis to be applied to the determination of the direct interaction function as has been used in the evaluation of the indirect correlation function.

The direct correlation functions of liquid He^4 over most of the liquid temperature interval have been obtained by Goldstein[22] using the x-ray scattering data of Reekie.[23] He has shown these functions to satisfy two types of integral tests which proves their over-all character.

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[21] L. Goldstein, op. cit., p.2.

[22] L. Goldstein, Phys. Rev. 100, 981 (1955).

[23] J. Reekie and T. S. Hutchison, Phys. Rev. 92, 827 (1953); C.F.A. Beaumont and J. Reekie, Proc. Roy. Soc. (London) A228, 363 (1955).

DISCUSSION

The x-ray scattering data of Eisenstein[24] for argon has been used to calculate the direct correlation function f(r,T) for four of the curves listed in Figure 1. Three curves, numbers 1, 4, and 6, represent argon in the liquid state. Curve number six is the closest in the liquid state to the critical point. Curve number 7 is the curve closest to the critical point in the vapor state.

The direct correlation functions for the above mentioned curves are shown in figures 2, 3, 4, and 5. The space integrals $F(r,T) = \int 4\pi r^2 f(r,T)dr$ for the curves are shown in figures 6, 7, 8, and 9. It is shown in the next section of this paper that the isothermal compressibility can be calculated from the space integrals F(r,T).

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[24] A. Eisenstein and N. S. Gingrich, op. cit., p.3.

THEORY

The main features of the Ornstein-Zernike static liquid model and the derivation of the direct interaction function in terms of the available x-ray scattering data have been presented by Goldstein[25].

First let us proceed with a derivation of the indirect correlation function in terms of the direct correlation function.[26]

Let V = Volume of the sample.

N_V = Total number of molecules in volume V.

$\overline{N}_V$ = Average number of molecules in volume V.

ΔN_V = Random fluctuation of the molecules in volume V.

N_j = Total number of molecules in cell j.

$\overline{N}_j$ = Average number of molecules in cell j.

ΔN_j = Random fluctuation of the molecules in cell j.

dv_j = Volume of cell j.

j designate a homogeneous cell of molecules within volume V.

Let us define the average of the fluctuation of the number of molecules in the kth cell due to the fluctuation in the jth cell by introducing $g(r_{jk})$, a function of the distance between the two cells such that

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[25] L. Goldstein, Phys. Rev. 84, 466 (1951).

[26] This development was suggested by Dr. Louis H. Lund, Professor of Physics at the Missouri School of Mines.

$$(2) \qquad \overline{\Delta N}_k|_j = \underset{j \neq k}{g(r_jk)dv_k\Delta N_j} \, ,$$

where r_{jk} is equal to the distance from the jth to the kth cell. We see that this average fluctuation depends upon the fluctuation in the jth, the volume in the kth, and a function of the distance between the two cells.

We introduce the direct correlation function $f(r_{jk})$ by considering the average fluctuation in the kth cell due directly to the effect of the fluctuations in all other cells, which is given by

$$(3) \qquad \overline{\Delta N}_k = \sum_{\substack{j \\ j \neq k}} f(r_{jk})\, dv_k\, \Delta N_j \, .$$

From equation (3) we obtain the very important concept

$$(4) \qquad \overline{\Delta N}_k|_i = \sum_{\substack{j \\ j \neq k \neq i}} f(r_{jk})\, dv_k\, \overline{\Delta N}_j|_i + f(r_{ik})\, dv_k\, \Delta N_i \, ,$$

which says that the average fluctuation of the number of molecules in the kth cell due to the ith cell is equal to the linear superposition of the effect of the average fluctuations in the jth cell due to the ith plus the direct effect of the fluctuation in the ith cell.

Equation (2) tells us that $\overline{\Delta N}_j|_i = g(r_{ij})dv_j\Delta N_i$. Substituting this in equation (4) we obtain

$$\overline{\Delta N}_k|_i = \underset{i \neq k}{g(r_{ik})dv_k\Delta N_i} = \sum_{\substack{j \\ j \neq k \neq i}} f(r_{jk})dv_k\, g(r_{ij})dv_j\Delta N_i + f(r_{ik})dv_k\Delta N_i \, .$$

Solving for $g(r_{ik})$ leads to

$$(5) \quad g(r_{ik}) = \sum_{\substack{j \neq k \neq i}} {}_j f(r_{jk}) g(r_{ij}) dv_j + f(r_{ik}).$$

In the continuum representation and as a function of distance and temperature Equation (5) becomes

$$(6) \quad g(\bar{r},T) = \int f(\bar{r}-\bar{r}',T)\, g(\bar{r}',T)\, dv' + f(\bar{r},T) .$$

This states that the indirect correlation between a molecule at the origin and one at a distance r is equal to the direct interaction $f(\bar{r},T)$ with the molecule at r plus the sum of the correlations with those molecules surrounding the origin which are caused by their direct interaction with the molecule at r. It is this relation which is fundamental to the Ornstein-Zernike static liquid model.

It is possible to express the direct interaction function in terms of the coherent scattering intensity data of the liquid. To do this we multiply both sides of equation (6) by $\cos(\bar{r}\cdot\Delta\bar{k})$, where

$$\left|\Delta\bar{k}\right| = 2\pi\left|\bar{k}\right|/\lambda = 2\pi\left|\bar{S} - \bar{S}_o\right|/\lambda = 4\pi \sin\theta/\lambda .$$

$\bar{S}_o$ is a unit vector along the incident x-ray, $\bar{S}$ is a unit vector along the scattered x-ray and 2θ is the scattering angle. Integrating over the liquid volume or the whole space we obtain

$$(7) \quad G(\Delta k,T) = F(\Delta k,T) \left[1 - F(\Delta k,T)\right]^{-1}$$

where

$$G(\Delta k,T) = \int \cos(\bar{r}\cdot\Delta\bar{k})\ g(r,T)\ dv(r)\ ,$$

$$F(\Delta k,T) = \int \cos(\bar{r}\cdot\Delta\bar{k})\ f(r,T)\ dv(r)\ . \tag{8}$$

We may rewrite equation (8) by averaging $\cos(\bar{r}\cdot\Delta\bar{k})$ over all solid angle. Then

$$F(\Delta k,T) = \int_0^\infty 4\pi r^2 f(r,T)\ \frac{\sin(r\Delta k)}{r\Delta k}\ dr\ ,$$

$$G(\Delta k,T) = \int_0^\infty 4\pi r^2 g(r,T)\ \frac{\sin(r\Delta k)}{r\Delta k}\ dr\ . \tag{9}$$

Gingrich[27] has shown that the intensity of coherently scattered x-rays (I_{eu}) by a liquid is given by

$$I_{eu} = Nf^2\left[1 + \int_0^\infty 4\pi r^2\ g(r,T)\ \frac{\sin(r\Delta k)}{r\Delta k}\ dr\right]\ , \tag{10}$$

where f is called the atomic structure factor and is determined by the distribution of the electrons in the atom and N is equal to the number of atoms in the liquid volume. Equation (10) becomes, with equations (7) and (9),

$$\frac{I_{eu}}{Nf^2} = 1 + G(\Delta k,T) = \left[1 - F(\Delta k,T)\right]^{-1}\ . \tag{11}$$

Solving for $F(\Delta k,T)$ and using equation (9) again, we obtain

$$F(\Delta k,T) = 1 - (I_{eu}/Nf^2)^{-1}$$

$$4\pi\int_0^\infty r^2 f(r,T)\ \frac{\sin(r\Delta k)}{r\Delta k}\ dr = 1 - (I_{eu}/Nf^2)^{-1}\ . \tag{12}$$

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[27] N. S. Gingrich, op. cit., p.2.

Applying the Fourier transform theorem to equation (12) we arrive at

$$(13)\quad f(r,T) = 1/2\pi^2 r \int_0^\infty \left[1 - (I_{eu}/Nf^2)^{-1}\right] \Delta k \sin(r\Delta k)\, d(\Delta k).$$

Equation (13) may be rearranged into a more useful form by writing $i(\Delta k) = I_{eu}/Nf^2 - 1$, then

$$(14)\quad f(r,T) = 1/2\pi^2 r \int_0^\infty \frac{\Delta k\ i(\Delta k)}{i(\Delta k) + 1} \sin(r\Delta k)\, d(\Delta k).$$

We shall now proceed to derive the relation which exists between the direct interaction function $f(r,T)$ and the isothermal compressibility β.

Let us define the mean square of the fluctuation of the number of molecules in volume V by

$$(15)\quad \Delta N_V^2 = \sum_j \sum_k \overline{\Delta N_j\ \Delta N_k} = \underset{j\,=\,k}{\sum_j \overline{\Delta N}_j^2} + \underset{j\,\neq\,k}{\sum_j\sum_k \overline{\Delta N_j\ \Delta N_k}}\ .$$

It can be shown[28] from fluctuation theory that the mean square of the fluctuation in cell j classically is equal to the average number of molecules in cell j, i. e.,

$$(16)\quad \underset{j\,=\,k}{\sum_j \overline{\Delta N}_j^2} = \sum_j \overline{N}_j = \overline{N}_V\ .$$

The average of the fluctuation in the kth cell due to the jth and the fluctuation in the jth is

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[28] J. Slater, Introduction to Chemical Physics, N.Y., McGraw-Hill, (1939).

(17) $$\overline{\Delta N_k|_j\,\Delta N_j} = \overline{g(r_{jk})dv_k \Delta N_j \Delta N_j} = g(r_{jk})dv_k\,\overline{\Delta N_j}^2 .$$

Since $\overline{\Delta N}_j{}^2 = \overline{N}_j = N\,dv_j$, where N = average number of molecules per unit volume, then equation (15) can be written as

(18) $$\overline{\Delta N}_V{}^2 = \overline{N}_V + \sum_j \sum_k g(r_{jk})\ dv_k\ N\ dv_j$$
$$j \neq k$$

$$= \overline{N}_V + \overline{N}_V \sum g(r)\ dv .$$

Writing equation (18) in the continuum representation we get

(19) $$\overline{\Delta N}_V{}^2 = \overline{N}_V + \overline{N}_V \int g(r)\ dv .$$

Let

(20) $$G(r,T) = \int g(r,T)\ dv; \quad F(r,T) = \int f(r,T)\ dv,$$

then

(21) $$\overline{\Delta N}_V{}^2 = \overline{N}_V \left[1 + G(r,T) \right] .$$

Multiplying both sides of equation (6) by dv(r) and integrating over the whole space, one obtains

(22) $$1 + G(r,T) = \left[1 - F(r,T) \right]^{-1} = \overline{\Delta N}_V{}^2 / \overline{N}_V .$$

In a large volume and as long as the state of the fluid is not the critical state, $\overline{\Delta N}_V{}^2 / \overline{N}_V$ is found by statistical thermodynamics[29] to be

(23) $$\overline{\Delta N}_V{}^2 / \overline{N}_V = NKT\beta ,$$

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[29] M. v. Smoluchowski, Ann. Physik 25, 205 (1908).

where K is Boltzman's constant and β is the isothermal compressibility at temperature T. Therefore,

$$(24) \quad \int_0^\infty f(r,T)\ 4\pi r^2 \ dr = \left[1 - NKT\beta\right]^{-1}$$

$$F(r,T) = \left[1 - NKT\beta\right]^{-1}$$

This provides us with a means of checking f(r,T) as determined from the x-ray scattering data.

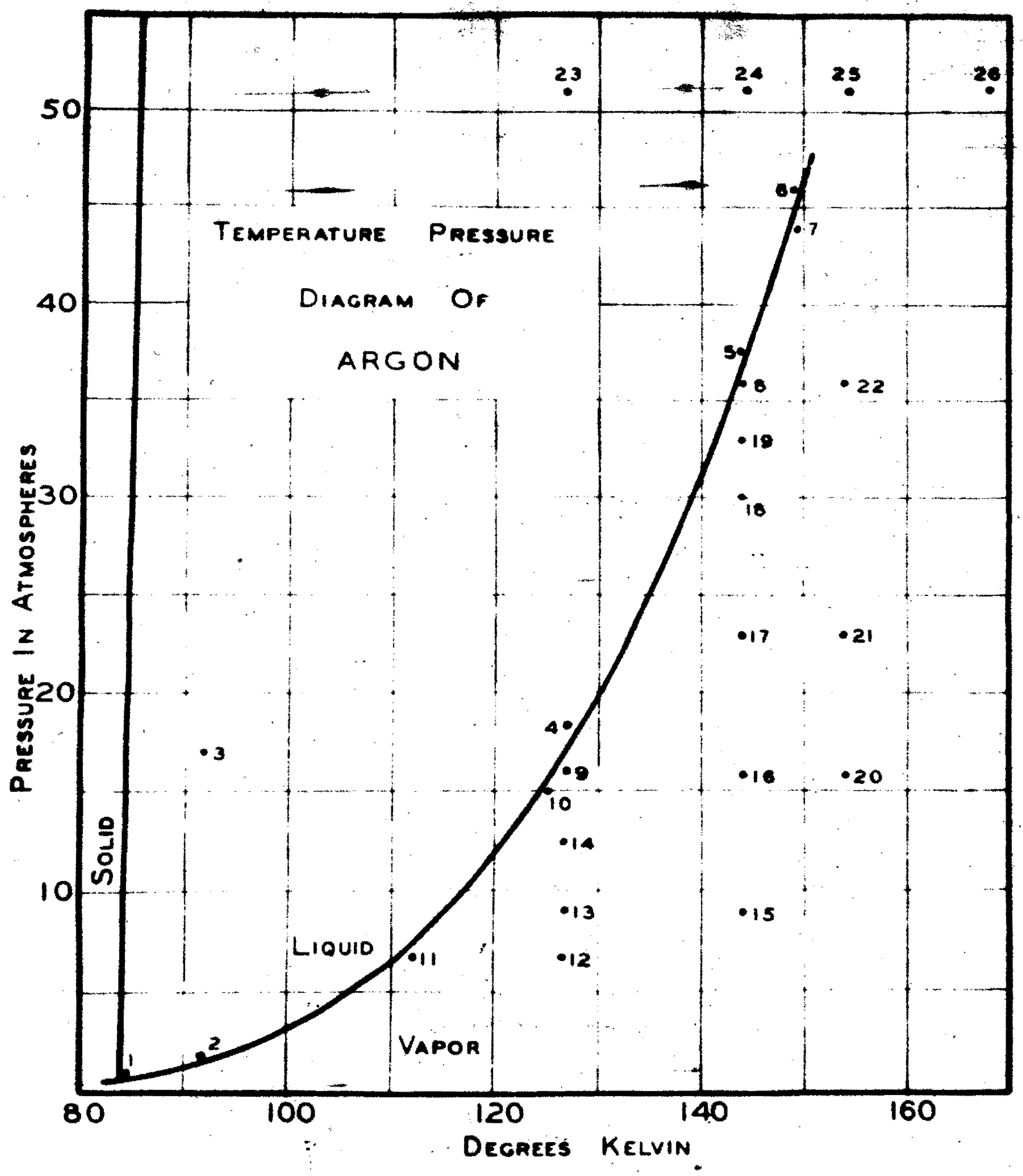

Figure 1. Pressure-Temperature for argon with datum points corresponding to x-ray scattering patterns.

APPLICATION OF THEORY

The direct correlation function f(r,T) was calculated for liquid argon at temperatures and pressures as indicated by datum points 1, 4, 6, and 7 in figure 1 on the liquid-vapor transition curve. Using equation (14) values of f(r,T) were calculated at intervals of 0.5 angstroms in r from 0.5 to 7 angstroms, and intervals of 1 angstrom in r from 7 to 20 angstroms. A value of r was chosen and then kept constant while values of Δk and $i(\Delta k)$ were inserted into the equation. The integrand was then tabulated, graphed and planimetered for the area under the curve which represented the value of $2\pi^2 r$ f(r,T). Dividing by $2\pi^2 r$ then gave a value of f(r,T). This was done for datum points 1 and 4 for values of r equal 0.5 to 7 angstroms. The values of $i(\Delta k)$ were obtained[30] in intervals of .01 A^{-1} for $\Delta k/4\pi$.

The values of f(r,T) tend to become less accurate for increasing values of r. At 10 angstroms for example, there are only 2.5 integration intervals per half cycle of the sine function in the integrand of equation (14). The values of f(r,T) for datum points 1 and 4 for r from 7 to 20 angstroms, and for datum points 6 and 7 for r from 0.5 to 20 angstroms were calculated by a method[31] which did not have the limitations arising from the decreasing accuracy of

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[30] Eisenstein, A., Ph. D. Dissertation, University of Missouri, Columbia, Missouri, June, 1942.

[31] L. Goldstein and J. Reekie, Phys. Rev. 98, 857 (1955).

integrations at large separations. Let

$$(25) \quad g(\Delta k,T) = \frac{\Delta k\ i(\Delta k)}{i(\Delta k) + 1}$$

and rewrite equation (14) as

$$(26) \quad f(r,T) = 1/2\pi^2 r \int_0^\infty g(\Delta k,T) \sin(r\Delta k)\, d(\Delta k) .$$

Actually the interval of integration is finite. Dividing this finite interval into N equal parts w, we obtain

$$(27) \quad f(r,T) = 1/2\pi^2 r \left[\int_0^w g(\Delta k,T)\sin(r\Delta k)d(\Delta k) + \int_w^{2w} g(\Delta k,T)\sin(r\Delta k)d(\Delta k) + \cdots\right] .$$

If the function $g(\Delta k,T)$ varies slowly in the interval w, it may be replaced by $\bar{g}\left[(n-1)w,nw\right]$ its value in the middle of the interval w. Then

$$(28) \quad f(r,T) = 1/2\pi^2 r \left[\bar{g}(0,w) \int_0^w \sin(r\Delta k)d(\Delta k) + \bar{g}(w,2w)\int_w^{2w} \sin(r\Delta k)d(\Delta k) + \cdots\right] .$$

Integrating the sine function, we may write, with good approximation,

$$f(r,T) = 1/2\pi^2 r^2 \left[-\bar{g}(0,w)\cos(r\Delta k)\Big|_0^w - \bar{g}(w,2w)\cos(r\Delta k)\Big|_w^{2w} - \cdots\right]$$

$$= 1/2\pi^2 r^2 \left\{\bar{g}(0,w) + \left[\bar{g}(w,2w) - \bar{g}(0,w)\right]\cos(rw) + \left[\bar{g}(2w,3w) - \bar{g}(w,2w)\right]\cos(r2w) + \cdots\right\}$$

$$(29) \quad f(r,T) = 1/2\pi^2 r^2 \left\{\bar{g}_1 + \sum_{n=1}^{N}(\bar{g}_{n+1} - \bar{g}_n)\cos(nrw)\right\},$$

where $\bar{g}_n = \bar{g}\left[(n - 1)w, nw\right]$.

As in the other method a value of r was chosen and then kept constant while values of $\bar{g}_n$ were inserted into equation (29), tabulated and summed. Dividing by $2\pi^2 r^2$ gave a value for f(r,T). The curves f(r,T) versus r are shown in figures 2, 3, 4 and 5.

The direct correlation functions were submitted to an integral check available for the functions. Using equation (24), the values of F(r,T) were calculated over the r range of 0 to 20 angstroms for the four functions of f(r,T). The values of f(r,T) for a given value of r, were multiplied by the factor $4\pi r^2$ and tabulated. The area under the curve for different values of r was determined by use of the trapezoidal rule. F(r,T) versus r are shown in figures 6, 7, 8, and 9. The values of $\lim_{r \to} F(r,T)$ or $\left[1 - (NKTB)^{-1}\right]$ are also indicated in figures 6 and 7.

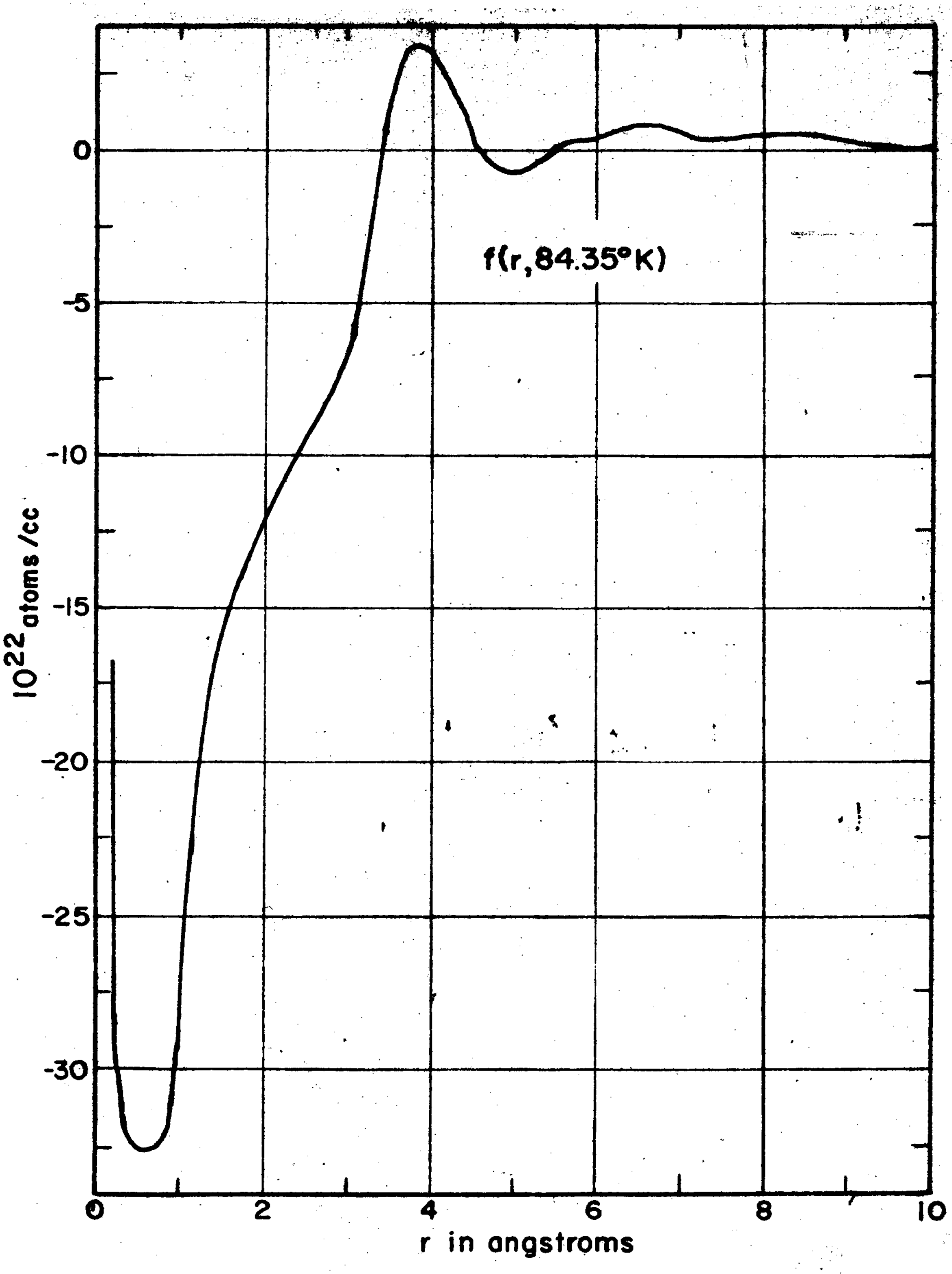

Figure 2. Direct correlation function f(r,84.35°K) vs. the interatomic separation corresponding to datum point 1.

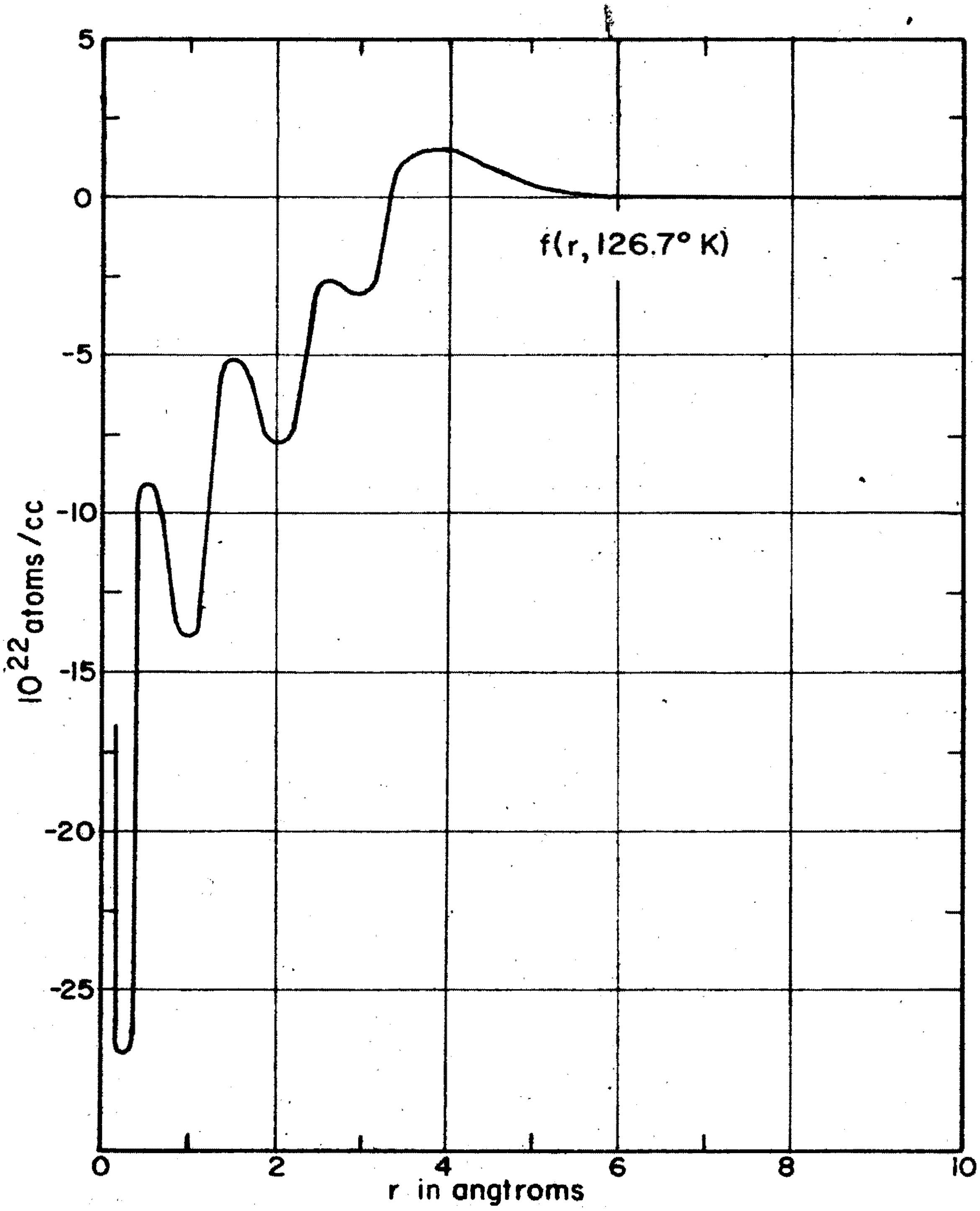

Figure 3. Direct correlation function f(r,126.7°K) vs. the interatomic separation corresponding to datum point 4.

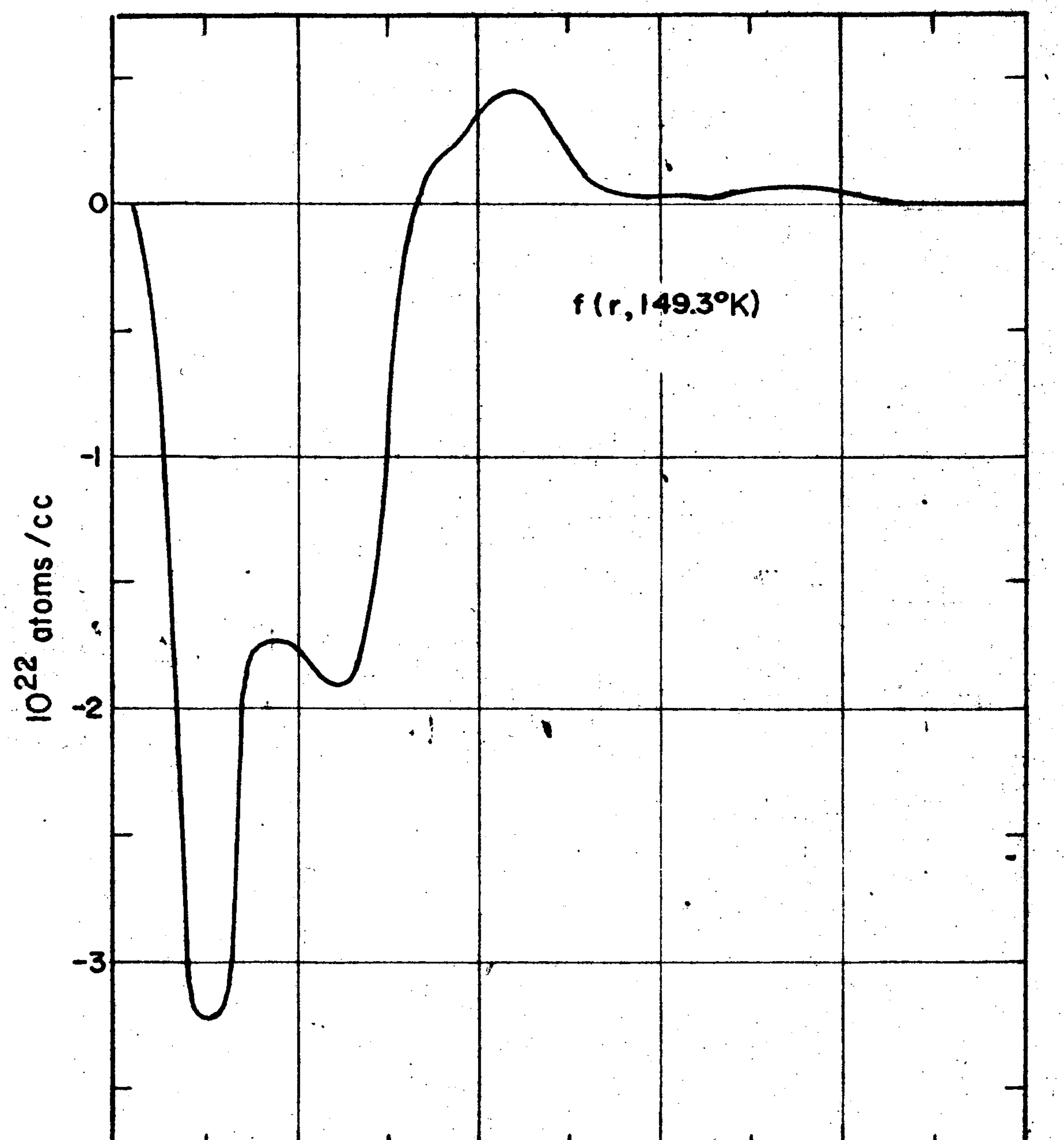

Figure 4. Direct correlation function f(r,149.3°K) vs. the interatomic separation corresponding to datum point 6.

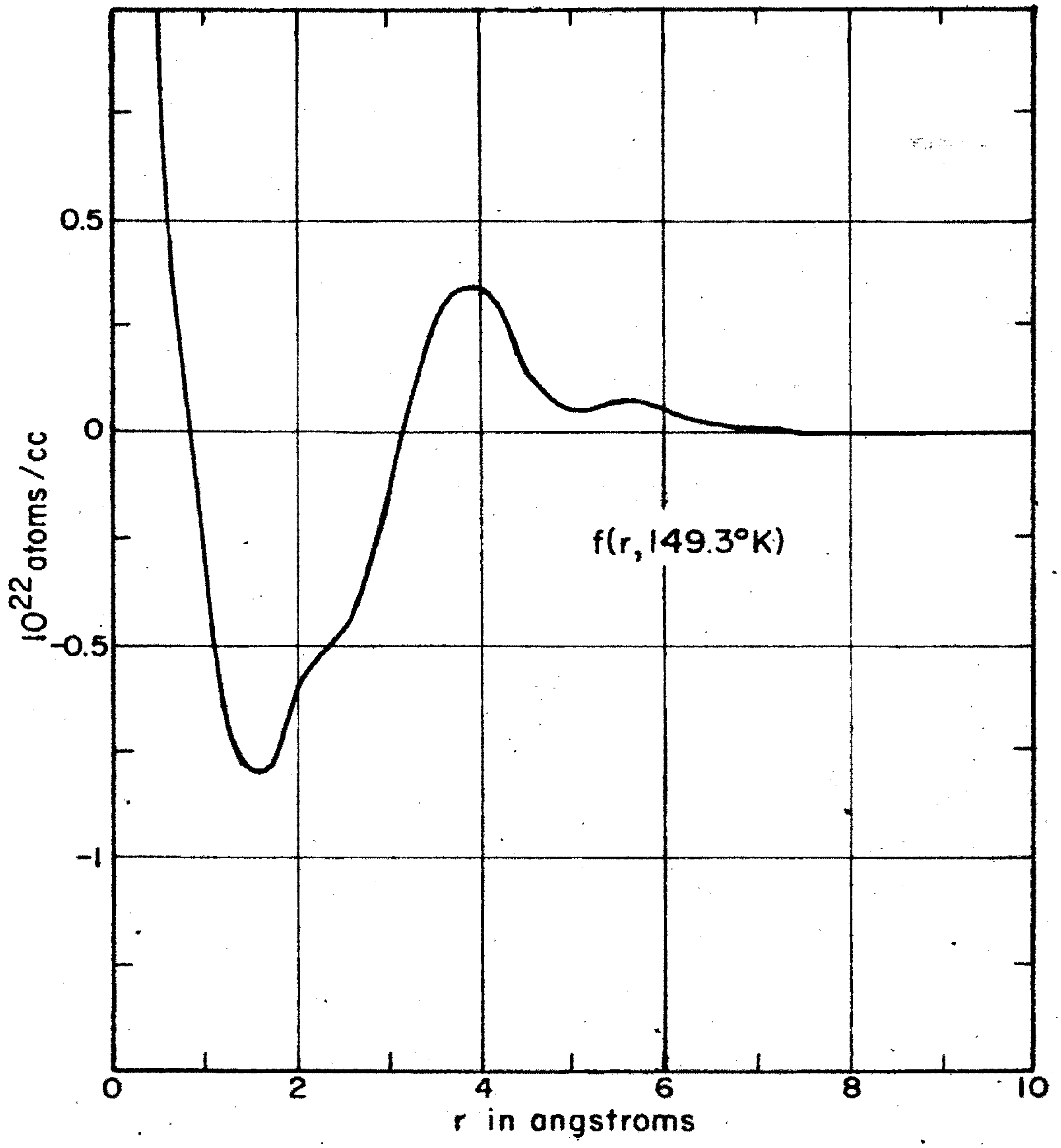

Figure 5. Direct correlation function f(r, 149.3°K) vs. the interatomic separation corresponding to datum point 7.

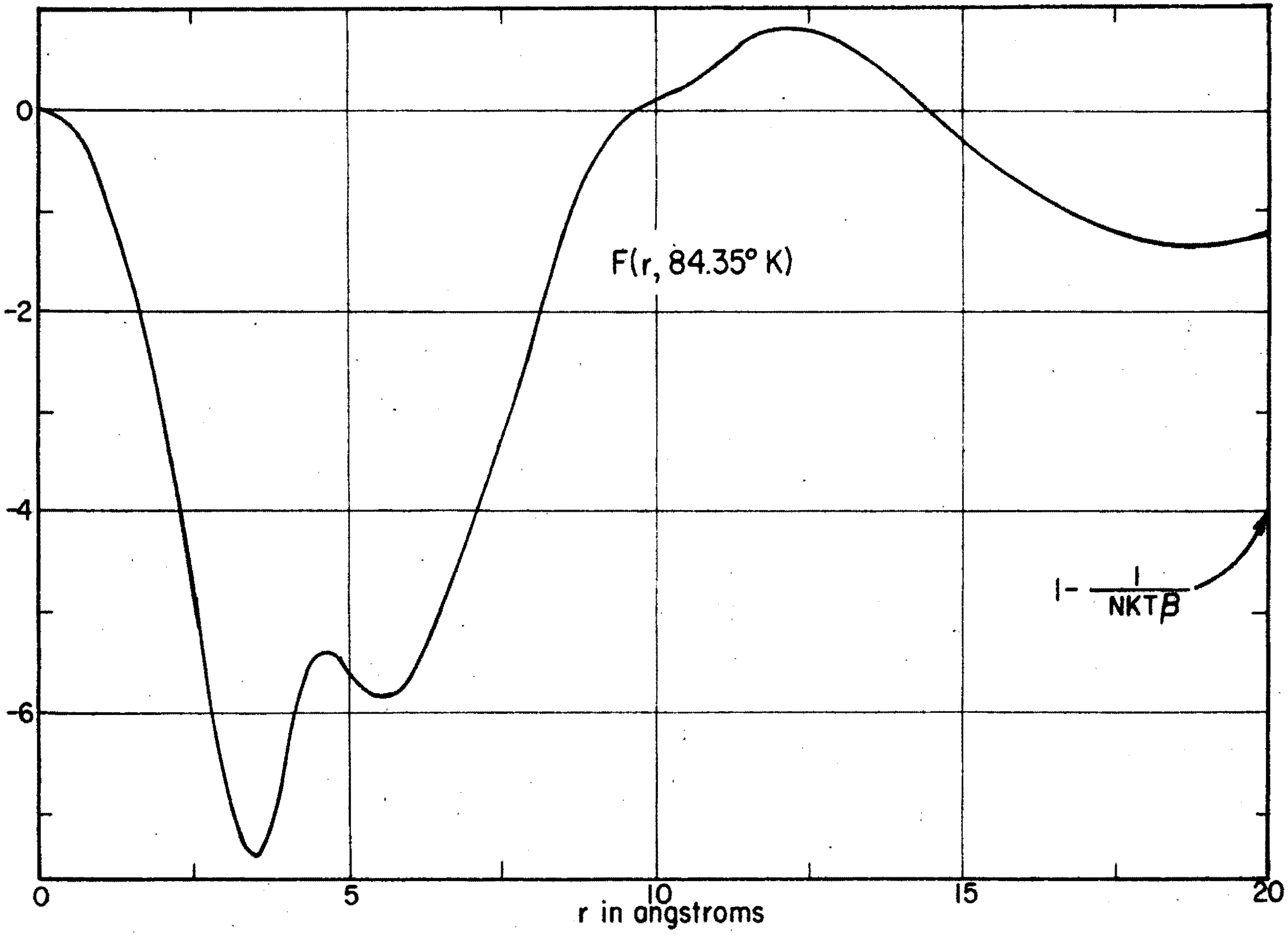

Figure 6. Space integral F(r,84.35°K) vs. the interatomic separation corresponding to datum point 1.

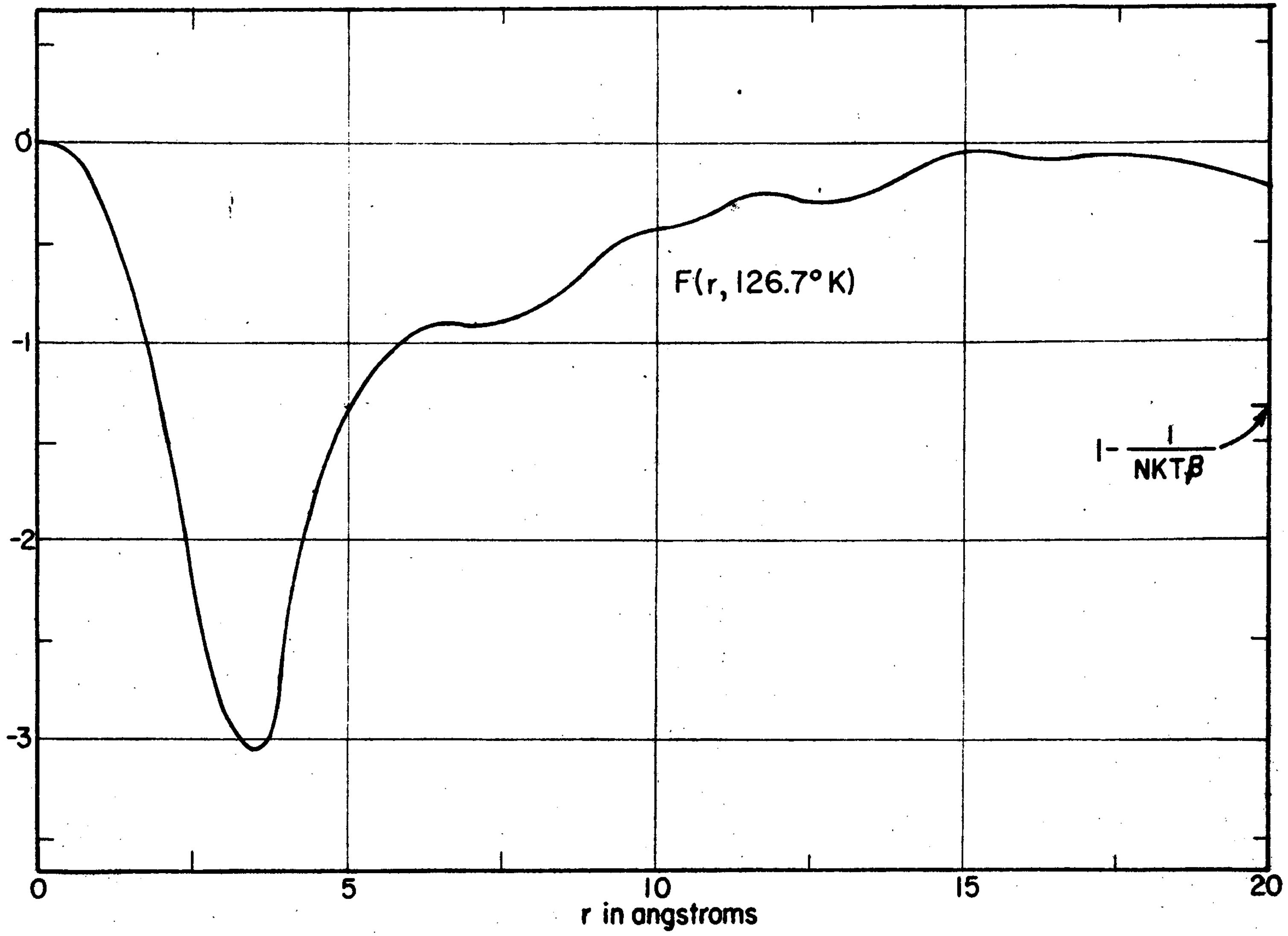

Figure 7. Space integral F(r,126.7°K) vs. the interatomic separation corresponding to datum point 4.

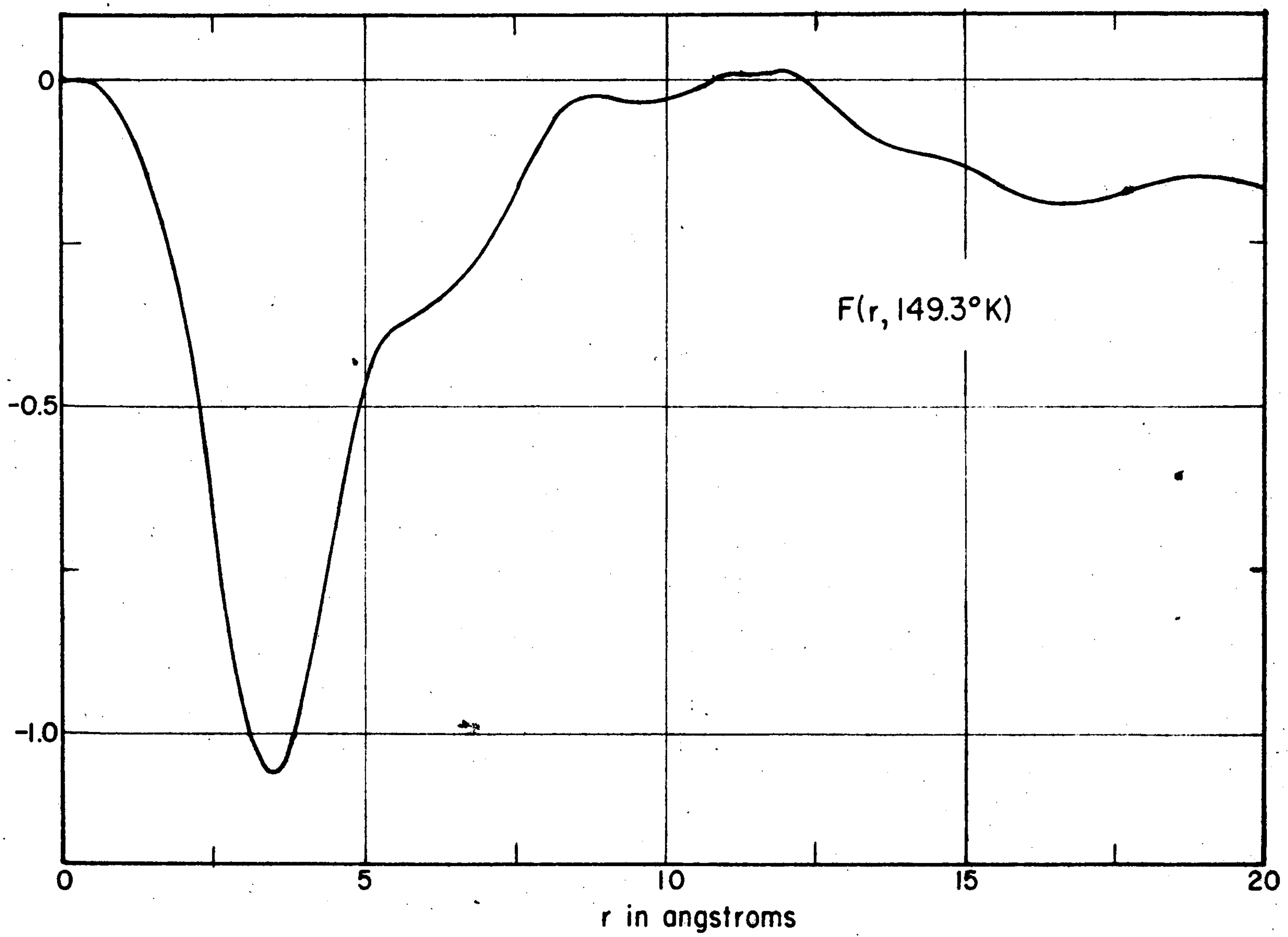

Figure 8. Space integral F(r, 149.3°K) vs. the interatomic separation corresponding to datum point 6.

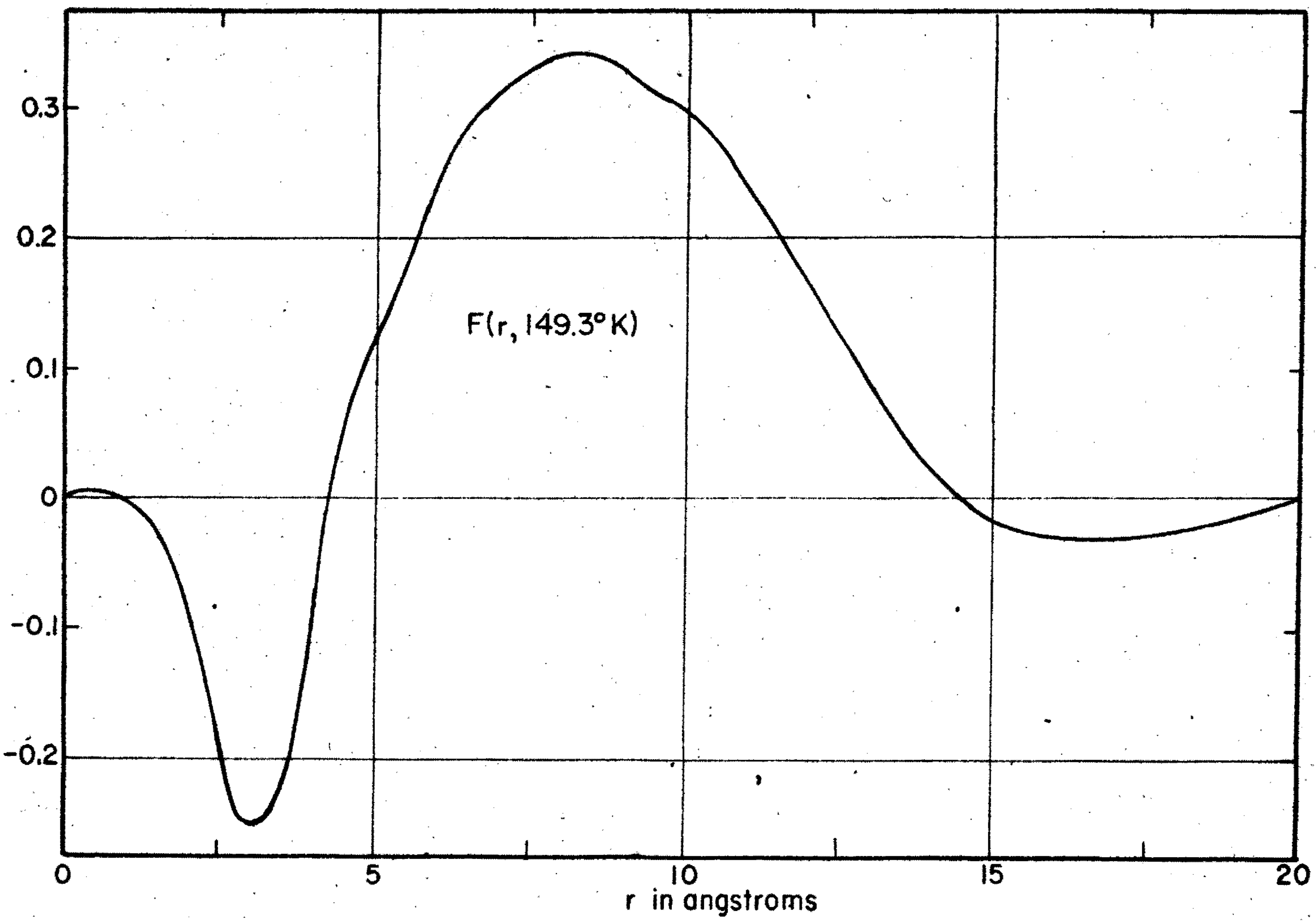

Figure 9. Space integral F(r,149.3°K) vs. the interatomic separation corresponding to datum point 7.

CONCLUSION

The x-ray scattering data for liquid argon has been used to calculate the direct correlation function f(r,T), proposed by Ornstein and Zernike, over a wide range of temperature. The values of f(r,T) versus r are shown in figures 2, 3, 4, and 5 for the temperatures 84.35°K, 126.7°K, 149.3°K (liquid) and 149.3°K (vapor) respectively. The graphs extend only to separations of 10 angstroms. At larger distances these functions are a very small fraction of their value at closer separations. The principal minimum of the functions was found to be less at higher temperatures than at lower temperatures. The anomalous behavior of the function f(r,T) for datum point 4 near the origin is not understood. It should be pointed out, however, that in contrast to the indirect correlation functions g(r,T), the direct correlation function f(r,T) do not have any precise physical meaning at or near the origin. As can be noted from their graphs the functions f(r,T) are of relatively short-range character.

Figures 6, 7, 8, and 9 show the generalized integrals F(r,T) versus r. The values of lim F(r,T) or $\left[1 - (NKTB)^{-1}\right]$ are also indicated on the graphs for datum points 1 and 4. The space integrals for these two temperatures satisfy their limiting values at separations of 5 and 7 angstroms respectively. This might be interpreted as the range of the functions f(r,T) at these temperatures since the interatomic force between two argon atoms[32] has a range of approximately 9 angstroms. The

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[32] Hirschelder, Curtiss, and Bird, Molecular Theory of Gas and Liquids, N.Y. Wiley, (1954).

space integrals do not approach their limiting value at large r. This is not to be expected inasmuch as the rigorous interaction functions are unknown. The functions $f(r,T)$, being derived from x-ray scattering data, are the best approximation known at this time.

As the temperature approaches the critical temperature T_c of the liquid, the space integrals are shown by Goldstein[33] to approach unity, explicitly

$$\lim_{T \to T_c} F(r,T) = 1.$$

Datum points 6 and 7 represent curves near the critical temperature. The approximate limiting values of the space integrals for these curves as calculated from their compressibility[34] are 0.3 and 0.8 respectively. These space integrals do not reach their limiting value for values of r from 0 to 20 angstroms, nor do they tend to approach unity.

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33. L. Goldstein, Phys. Rev. <u>84</u>, 466 (1951).

34. G. H. Vineyard, Phys. Rev. <u>74</u>, 1076 (1948).

SUMMARY

Direct correlation functions f(r,T) were calculated from four x-ray scattering patterns of liquid argon at temperatures of 84.3°K, 126.7°K, 149.3°K (liquid) and 149.3°K (vapor). The graphs of these functions indicated that they were of short-range character. Three of the four curves were very similar in shape. No explanation is given for the irregularities near the origin in the fourth curve.

For the two curves, whose temperature and pressure was not near the critical point, the space integrals of the correlation functions satisfy their limiting value at distances of from 5 to 7 angstroms.

The direct correlation functions as calculated here for liquid argon seem to agree favorably with the results of Goldstein[35] for liquid He^4.

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[35] L. Goldstein, Phys. Rev. 100, 981 (1955)

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VITA

Arthur Reetz, Jr. was born April 8, 1929, in Yankton, South Dakota, the son of Arthur and Margaret Reetz. He received his elementary education in the public schools of Yankton and was graduated from Yankton High School in May, 1947.

In September, 1948, he enrolled in the State University of Iowa as an engineering student. He transferred to the University of South Dakota in February, 1950, and received a B. S. in Education from that same institution in June, 1951.

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The writer was married to Marlene Zimmerman, also of Yankton, on July 30, 1950. They have three children, two boys and a girl.