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AN EQUATION OF STATE OF GASES AT HIGH TEMPERATURES AND DENSITIES

by

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AN EQUATION OF STATE OF GASES AT HIGH TEMPERATURES AND DENSITIES*

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ABSTRACT

An equation of state is obtained in closed form for a gas composed of molecules with Lennard-Jones $(n, \frac{1}{2}n)$ potentials. It is useful at temperatures above about 12 (ϵ/k), where $-\epsilon$ is the minimum energy of interaction and at all densities at which the equilibrium state is a fluid. It is derived by summing over all the cluster integrals of the virial expansion that occur in the approximation for the pair distribution function proposed by Percus and Yevick. Each cluster integral is represented correctly to terms of the order of n^{-1}.

The equation agrees well with machine calculations of the pressure of dense gases for $n = \infty$ and $n = 12$, with static measurements of the compression of gases at high reduced temperatures, and with some preliminary measurements of the density of argon compressed by shock-waves to pressures in the range 100-200 kb.

AUTHOR

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AN EQUATION OF STATE OF GASES AT HIGH TEMPERATURES AND DENSITIES

1. Introduction

In 1958 Percus and Yevick suggested a new approximation in the theory of fluids which has since been derived and expressed in several ways [1 - 5] . The original formulation, which is used here, leads to an expansion of the pair distribution function in powers of the density, the coefficients of which are some, but not all, of the open cluster integrals of the exact expansion of Mayer and Montroll [6] . Such a series is equivalent to an expansion of the pressure in powers of the density in which the coefficients are a selection from the complete set of irreducible cluster integrals. These approximate virial coefficients are of a particularly simple form for an assembly of hard spheres for which the expansion can be summed over all powers of the density to obtain the equation of state in closed form. Wertheim [4] and Thiele [5] have shown recently that this closed form can be also obtained directly from the equations of Percus and Yevick without recourse to an expansion in powers of the density.

These results are extended here to a gas between whose molecules there is a Lennard-Jones $(n, \frac{1}{2}n)$ potential. The extension can be made only at temperatures where the repulsive forces are dominant, that is, at temperatures above about $12\,(\epsilon/k)$ where $-\epsilon$ is the minimum energy of interaction. The equation of state can be used for the calculation of the properties of fluids compressed by strong shock-waves and of the properties of the products of the detonation of explosives.

The Lennard-Jones $(n, \frac{1}{2}n)$ potential for a pair of molecules separated by a distance R is

$$u(R) = \epsilon\left[\left(\frac{R_m}{R}\right)^{n} - 2\left(\frac{R_m}{R}\right)^{\frac{1}{2}n}\right] \qquad (n>6) \qquad (1.1)$$

[redacted]

2. The Cluster Integrals

The expansion of the pair distribution function $n_2(R_{12})$ in powers of the density has coefficients that are functions of the separation of molecules 1 and 2. Each coefficient is obtained by integrating factors $f(R_{ij})$ over all positions of one or more additional molecules, where

$$f(R_{ij}) = \exp\left[-u(R_{ij})/kT\right] - 1 \tag{2.1}$$

Thus the coefficient of the fourth power of the density is the cluster integral shown schematically as c3 in Figure 1. The coefficient of the fifth power is formed from three cluster integrals, shown schematically as d4 , d5 and d6 . The compressibility is obtained by substituting $n_2(R_{12})$ into the exact equation of Ornstein and Zernike,

$$kT\left(\frac{\partial(N/V)}{\partial p}\right)_T = 1 + \left(\frac{N}{V}\right)^{-1}\int\left[n_2(R_{12}) - \left(\frac{N}{V}\right)^2\right] d(\underline{R}_2 - \underline{R}_1) \tag{2.2}$$

where (N/V) is the number density. This equation is inverted, expanded by the binomial theorem, and integrated with respect to density to obtain the familiar virial expansion for the pressure, whose coefficients are C3 , D4 , D5 , D6 etc. of Figure 1. (The use of (2.2) is more accurate for hard spheres than the direct calculation of p from the virial theorem, for reasons which have been discussed elsewhere [7]). The approximation of Percus and Yevick for $n_2(R_{12})$ can be expressed [1] by the rule that only those open cluster integrals are included that can be written either as simple chains from molecule 1 to molecule 2 (eg. c3 and d4) or which can be formed from simple chains by introducing interior bonds that do not cross each other. That is, terms such as d5 are included, but d6 is not. The omission of d6 from $n_2(R)$ leads to the omission of D6 from the pressure. The terms that are retained in p are those whose calculation is the simplest. If the molecules are hard spheres of diameter R_m , that is, if n becomes infinite in (1.1), then all the required cluster integrals are rational fractions of the appropriate power of b_m, where

$$b_m = \frac{2}{3}\pi N R_m^3 \tag{2.3}$$

Rushbrooke [8] has recently calculated the first six coefficients

$$B = b_m \ , \quad C = \frac{5}{8} b_m^2 \ , \quad D = \frac{19}{64} b_m^3 \ , \quad E = \frac{31}{256} b_m^4 \ , \quad F = \frac{23}{512} b_m^5 \tag{2.4}$$

The second differences of the numerical parts of these coefficients are constant, hence the coefficients can be expressed as a quadratic function of the order, q, of the virial coefficient. If L_q is the q^{th} virial coefficient then the generalization of (2.4) is

$$L_q = \left[1 + \frac{3}{2}q(q - 1)\right] (b_m/4)^{q-1} \tag{2.5}$$

Substitution of (2.5) into the virial expansion gives a series which can be summed to the closed form

$$\frac{pV}{NRT} = \frac{1 + \xi + \xi^2}{(1 - \xi)^3} \tag{2.6}$$

where

$$\xi = b_m/4V \tag{2.7}$$

The second and third coefficients of (2.4)-(2.7) are correct, the fourth exceeds the true value [9] by a factor of 1.0346, and the fifth exceeds a value obtained by direct calculation [7] by a factor of 1.100.

3. The Lennard-Jones Potential

Two important features of the approximation of Percus and Yevick for the hard spheres are, first, that the virial expansion can be summed and, secondly, that the individual coefficients are unusually accurate. The first property is a consequence of the exclusion of all integrals, such as D6, in which the numerical coefficients of $(b_m)^{q-1}$ are irrational. All the clusters that are retained have integrands that are related to the volume common to two overlapping spheres. The integrand of C3 is just this volume, and the integrands of D4, D5 and of the admitted parts of E are such volumes integrated further between rational limits [7, 10]. Such simple results cannot be expected for a function as complicated as a Lennard-Jones potential, for which an exact expression can be obtained only for B. This is usually written as an infinite series of factorial functions. The limiting value of C at high temperatures can be expressed by these functions to an accuracy of terms of the order of n^{-3} only [11]. The limiting values of D4 and D5 have been obtained correct only to n^{-1} [12]. It is unlikely that an accuracy greater than n^{-1} can be achieved for any of the higher cluster integrals without recourse to numerical integration and hence with the loss of the power of summation. In this paper, therefore, the results previously obtained for D4 and D5 are first extended to lower temperatures and then applied to all clusters included in the approximation of Percus and Yevick.

All functions that occur in the integrands of C3, D4, D5 etc. are of the form

$$\int_b^a f(r)\, r^{j-1}\, dr \tag{3.1}$$

where r is a reduced distance

$$r = R/R_m \quad , \tag{3.2}$$

j is an exponent that lies in the range $(o < j < \tfrac{1}{2}n)$, and a and b are simple functions of the separations of some of the molecules in the cluster. If $f(r)$ can be approximated by a step-function,

$$\left.\begin{aligned} f(r) &= -1 \qquad & r < \rho \\ f(r) &= 0 \qquad & r > \rho \end{aligned}\right\} \tag{3.3}$$

then the evaluation of integrals such as (3.1) is no more difficult for a $(n,\frac{1}{2}n)$ potential than for hard spheres, and leads to similar rational expressions for the virial coefficients. However, this step is useful only if $f(r)$ can be accurately represented by the form (3.3), and if the distance ρ is independent of the exponent j in (3.1). If the temperature is high then $f(r)$ is almost equal to -1 at all separations less than about $x^{1/n}$, where x, the reciprocal of the reduced temperature, is small.

$$x = \tau^{-1} = \epsilon/kT \tag{3.4}$$

The function $f(r)$ is almost zero at larger separations. It is exactly zero at $r = 4^{-(1/n)}$, has a maximum of $(e^{x} - 1)$ at $r = 1$, and tends to zero as r becomes infinite. As before [12], let the distance ρ be defined by

$$\int_0^{\rho_j} (-1)\, r^{j-1}\, dr = \int_0^{\infty} f(r)\, r^{j-1}\, dr = x^{j/n}\, I^{n}_{(j/n)}(x) \tag{3.5}$$

The subscript j is added to ρ since, in general, the distance defined by (3.5) will depend upon this exponent. The integrals $I(x)$ were first studied by Lennard-Jones and their properties have recently been summarised [11]. From the first and third parts of (3.5),

$$(\rho_j)^{j} = -j\, x^{j/n}\, I^{n}_{(j/n)}(x) \tag{3.6}$$

Expand I(x) in powers of $x^{\frac{1}{2}}$

$$(\rho_j)^j = -j\, x^{j/n} \sum_{k=0}^{\infty} \frac{(\frac{1}{2}k - \frac{j}{n} - 1)!\,(2x^{1/2})^k}{n \cdot k!} \tag{3.7}$$

$$= j\, x^{j/n} \left[\frac{1}{j}\left(-\frac{j}{n}\right)! - \frac{1}{n} \sum_{k=1}^{\infty} \frac{(\frac{1}{2}k - \frac{j}{n} - 1)!\,(2x^{1/2})^k}{k!} \right] \tag{3.8}$$

This function can be written as a function of x , raised to the power j , by the neglect only of terms smaller than n^{-1} . The first factorial can be expanded around 0! [11] , and all terms (j/n) can be omitted from the sum.

$$(\rho_j)^j = j\, x^{j/n} \left[\frac{1}{j} + \frac{1}{n} F(x) \right] \tag{3.9}$$

$$= x^{j/n} \left[1 + n^{-1} F(x) \right]^j \tag{3.10}$$

where

$$F(x) = \gamma - \sum_{k=1}^{\infty} \frac{(\frac{1}{2}k - 1)!\,(2x^{1/2})^k}{k!} \tag{3.11}$$

$$= \gamma - 2(\pi x)^{1/2} \sum_{\ell=0}^{\infty} \frac{x^{\ell}}{(2\ell+1)\ell!} - \sum_{m=1}^{\infty} \frac{(m-1)!\,2^{2m}\,x^m}{(2m)!} \tag{3.12}$$

and γ is Euler's constant, 0.577216--. F(x) is closely related to, but cannot be obtained from, the series used to calculate B for a (n,½n) potential. It is tabulated in the Appendix. Thus ρ is independent of j (to terms of the order of n^{-1}) and can be written

$$\rho = x^{1/n}\left[1 + n^{-1} F(x)\right] \tag{3.13}$$

This distance is a measure of the effective range of the repulsive forces. If n is infinite then ρ is unity at all temperatures. If n is finite then ρ depends upon the temperature, both directly through $x^{1/n}$ and also through the effects of the attractive forces which enter through the sum in F(x) . In the limit of high temperatures $F(x) = \gamma$ and

$$\rho = x^{1/n}\left[1 + \gamma/n\right] \tag{3.14}$$

The equation of state can now be obtained at once from the results of Section 2 since, at each temperature, the molecules can be represented in every cluster integral by hard spheres of diameter ρ . The pressure is again given by (2.6) where ξ is now defined by

$$\xi = \left(\frac{b_m}{4V}\right) x^{3/n}\left[1 + \frac{1}{n} F(x)\right]^3 \tag{3.15}$$

The configuration energy of the gas, U^* , is obtained by the integration from zero to an arbitrary density of

$$\left(\frac{\partial U^*}{\partial V}\right)_T = -p + T\left(\frac{\partial p}{\partial T}\right)_V \tag{3.16}$$

It is given by

$$U^* = \phi(pv - NkT) \tag{3.17}$$

where

$$\phi = \frac{3}{n}\left[1 - G(x)\left(1 + n^{-1}F(x)\right)^{-1}\right] \tag{3.18}$$

$$G(x) = -x\frac{d}{dx}F(x) \tag{3.19}$$

$$= \frac{1}{2}\sum_{k=1}^{\infty}\frac{\left(\frac{1}{2}k-1\right)!\left(2x^{1/2}\right)^{k}}{(k-1)!} \tag{3.20}$$

$$= (\pi x)^{1/2}e^{x} + \sum_{m=1}^{\infty}\frac{m!\,2^{2m}x^{m}}{(2m)!} \tag{3.21}$$

$G(x)$ is also tabulated in the Appendix.

At high temperatures

$$U^{*} = \frac{3}{n}(pv - NkT) \tag{3.22}$$

This result is exact for molecules that repel as R^{-n}, since the intermolecular energy of such molecules is a simple multiple of the intermolecular virial, $\left[R.du(R)/dR\right]$

4. The Virial Coefficients

The q^{th} virial coefficient is now

$$L_q = \left[1 + \tfrac{3}{2}q(q-1)\right]\left(b_m/4\right)^{q-1} x^{3(q-1)/n}\left[1 + n^{-1}F(x)\right]^{3(q-1)} \tag{4.1}$$

If n is infinite these coefficients reduce to (2.4)-(2.7) at all temperatures. Figures 2-4 are a comparison of (4.1) with directly calculated coefficients [11-15] for the commonly used value of $n = 12$. A co-volume b_o is used instead of b_m in these Figures to conform with the usual convention.

$$b_o = 2^{-6/n} b_m \tag{4.2}$$

These Figures show also the coefficients calculated for a repulsive potential

$$u(R) = \lambda R^{-n} \quad , \quad \text{where} \quad \lambda = \epsilon R_m^n \tag{4.3}$$

It is seen that the coefficients calculated from (4.1) all lie below the true coefficients at high temperatures. The discrepancies are small and arise from the neglect of terms higher than n^{-1}. At low temperatures B exceeds the true value, whilst C and D lie below it. B is the cluster integral that is most sensitive to the effects of the attractive forces. Equation (4.1), with $q = 2$, is correct to n^{-1} in the sense that the exact expression for B [13] can be written in this form at all temperatures by neglecting only terms of the order of n^{-2}. However, in practice, the approximation is useful only for reduced temperatures above about 12. C is correct to the same order at high temperatures [11] whilst D and higher coefficients suffer a little from the neglect of certain clusters in the equations of Percus and Yevick. Nevertheless the agreement at high temperatures for all coefficients is most satisfactory.

This equation of state does not predict a liquid-vapour transition. All virial coefficients vanish at a Boyle temperature at which $F(x) = -n$. The configuration energy is positive at all densities if the temperature is above that of the maximum of the virial coefficients. This temperature is determined by

$$G(x) - n^{-1}.F(x) = 1 \tag{4.4}$$

This temperature is almost independent of n and is near $x = 0.12$ or $\tau = 8$.

5. Comparison with Experiment

This equation of state is compared below with three kinds of experiments. Calculations of the pressures of dense fluids have been made by Monte Carlo and other numerical techniques for $n = \infty$ and $n = 12$. A comparison with these results is a direct test of the equation. Static measurements have been made by conventional techniques of the pressures of helium, neon and hydrogen at high densities and reduced temperatures. These can be compared with theory if the parameters n , ϵ and R_m are known. However there is direct evidence [16] that this form of potential is not suitable at temperatures and densities when the repulsive forces are dominant, and so the comparison is not so direct a test of the equation as is the comparison with machine calculations. Finally, the equation is used to calculate the pressure and temperature of a gas compressed to a high density by a strong shock-wave.

Figure 5 is a comparison of (2.6) with the machine calculations of Alder and Wainwright for $n = \infty$. Two smooth curves have been drawn through their results, one of which is the fluid and the other of which is the solid state. There is probably a first-order transition at a reduced pressure of 4.2. It is seen that the approximation of Percus and Yevick is an excellent representation of pressure of the fluid phase but that it cannot (since all its virial coefficients are positive) show the transition to an ordered phase. It cannot be used, therefore, to represent the equilibrium state for $\xi > 0.45$, or $(pv/NkT) > 10$. There is also shown in the Figure an empirical equation of state which Kihara and Hikita [18] devised for molecules repelling as R^{-n} in order to represent the properties of the products of detonations, and which has been so used by Fickett, Wood and Salsburg [19] . This equation is correct at low and high densities (where it approaches the pressure of ordered phase) but is seriously low at the intermediate densities of the compressed fluid.

Figure 6 is a comparison of the equation of state for $n = 12$ with the Monte Carlo calculations of Wood and Parker [20] at two high temperatures. There is again good agreement although the calculated pressures may be a little high, as in Figure 5. However part of the small discrepancy at low densities may be in the Monte Carlo results since the calculated curve is almost indistinguishable from the correct four-term virial expansion for reduced densities below 0.7. The pressures at the highest densities shown would be about 30 kb (at $\tau = 20$) and 100 kb (at $\tau = 100$) for argon.

Figure 7 shows that a (12,6) potential recommended for helium [13, 21]

$$\underline{\text{Helium}} \qquad R_m = 2.88\ \mathring{\mathrm{A}}\ , \quad \epsilon/k = 10.8^{\circ}\mathrm{K} \qquad n = 12 \tag{5.1}$$

can be used with this equation of state to fit well the results of Wiebe, Gaddy and Heins [22], which extend to 1 kb. The excellence of the agreement at -70°C may be partly fortuitous, since no quantal corrections have been used.

There is no other gas for which measurements are available at so high a temperature and density. The next most suitable are neon and hydrogen, for which the measurements of Michels and his colleagues [23] extend to 150°C and 3 kb. This is a reduced temperature of about 11 for both gases and Figure 8 shows that the calculated pressures are a little too high when the following parameters are used [13, 21]

$$\underline{\text{Neon}} \qquad R_m = 3.09 \qquad \epsilon/k = 35.7^{\circ}\mathrm{K} \qquad n = 12 \tag{5.2}$$

$$\underline{\text{Hydrogen}} \quad R_m = 3.30 \qquad \epsilon/k = 37.0^{\circ}\mathrm{K} \qquad n = 12 \tag{5.3}$$

The fault is principally in the initial slopes of the isotherms, as is shown by the high calculated value of the second virial coefficient at this temperature (Figure 2).

Wackerle and Hughes [24] have measured the pressure and density of argon compressed by a strongshock-wave from an initial state of

$$p_o = 1\ \mathrm{kb} \qquad v_o = 41.1\ \mathrm{cm}^3\ \mathrm{mole}^{-1} \qquad T_o = 298^{\circ}\mathrm{K} \qquad U_o^{*} = -32.2\ \mathrm{kb\ cm}^3\ \mathrm{mole}^{-1}$$

The state of the gas after compression can be calculated by solving simultaneously the equation of state and Hugoniot's condition,

$$U - U_o + \tfrac{1}{2}(p + p_o)(V - V_o) = 0 \tag{5.4}$$

For argon, and this equation of state

$$U - U_o = U^* - U_o + \frac{3}{2} Nk(T - T_o) \tag{5.5}$$

$$= pV.\phi + NkT(\frac{3}{2} - \phi) - U_o^* - \frac{3}{2} NkT_o \tag{5.6}$$

where ϕ is defined by (3.18). This equation is useful if the reduced temperature of the shocked gas is above $12(\epsilon/k)$. It is not necessary for the initial state to be at so high a temperature if experimental values of p_o and U_o^* are used. This temperature is achieved in argon at pressures above about 40 kb with the initial state defined above. Figure 9 shows two calculated curves. One is for the commonly used (12,6) potential for argon [13, 21]

$$\underline{\text{Argon}} \qquad R_m = 3.83\ \text{Å} \qquad \epsilon/k = 119^\circ\text{K} \qquad n = 12 \tag{5.7}$$

and the second for a potential with the same R_m and (ϵ/k) but with $n = 9$

$$\underline{\text{Argon}} \qquad R_m = 3.83\ \text{Å} \qquad \epsilon/k = 119^\circ\text{K} \qquad n = 9 \tag{5.8}$$

Equation (5.7) exceeds the true potential for argon by a factor of between 4 and 10 for separations in the range 2.1 - 2.9 Å, which is the range of the mean separation of nearest neighbors in the shocked gas. The true potential at these separations was measured by Amdur and Mason [25] from the scattering of molecular beams, and is represented by (5.8). Amdur and Mason recommend a purely repulsive potential with an index of $n = 8.3$ for these separations but (5.8) appears to be the best potential that passes through their points and yet has a realistic value of R_m and (ϵ/k). The two experimental points of Wackerle and Hughes lie close to the Hugoniot curve calculated from this potential.

6. Conclusions

The comparisons of theory and experiment described in the last section were made without the introduction of any adjustable parameters. Their success suggests that this equation of state is substantially accurate at temperatures above $12(\epsilon/k)$ and at all pressures less than that of any transition to a solid phase, that is, below about 10^6 bar at these temperatures. It should therefore be reliable for calculations of the pressures of strongly shocked fluids and of the properties of the products of detonations. Its principal limitation is its restriction to a Lennard-Jones potential.

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Appendix

$\tau = x^{-1}$	F(x)	G(x)	$\tau = x^{-1}$	F(x)	G(x)
2	-3.570959	+3.477052	50	+0.032279	+0.296264
3	-2.452316	2.264765	60	0.083508	0.266375
4	-1.890323	1.730234	70	0.122792	0.243742
5	-1.543227	1.426019	80	0.154127	0.225868
6	-1.303763	1.227795	90	0.179861	0.211308
7	-1.126681	1.087347	100	0.201476	0.199161
8	-0.989338	0.982009	150	0.273769	0.159081
9	-0.879049	0.899689	200	0.316118	0.135993
10	-0.788110	0.833330	250	0.344706	0.120570
12	-0.645997	0.732371	300	0.365649	0.109356
14	-0.539117	0.658641	400	0.394818	0.093853
16	-0.455144	0.602033	500	0.414574	0.083431
18	-0.387014	0.556957	600	0.429080	0.075818
20	-0.330360	0.520054	700	0.440308	0.069948
25	-0.222302	0.451126	800	0.449331	0.065246
30	-0.144601	0.402741	900	0.456785	0.061371
35	-0.085382	0.366527	1000	0.463078	0.058107
40	-0.038375	0.338186	∞	0.577216	0.0

References

1 PERCUS, J. K. and YEVICK, G. J., 1958, Phys. Rev., 110, 1.

2 PERCUS, J. D., 1962, Phys. Rev. Letters, 8, 462.

3 STELL, G., 1963, Physica, 29, 517.

4 WERTHEIM, M. S., 1963, Phys. Rev. Letters, 10, 321.

5 THIELE, E., 1963, J. Chem. Phys., 39, 474.

6 MAYER, J. E. and MONTROLL, E., 1941, J. Chem. Phys., 9, 2.

7 ROWLINSON, J. S., Proc. Roy. Soc. A, submitted for publication.

8 RUSHBROOKE, G. S., 1963, J. Chem. Phys., 38, 1262.

9 VAN LAAR, J. J. 1899, Proc. Roy. Acad. Sci., Amsterdam, 1, 273; BOLTZMANN, L., 1899, ibid, 1, 398.

10 NIJBOER, B. R. A. and VAN HOVE, L., 1952, Phys. Rev., 85, 777.

11 ROWLINSON, J. S. 1963, Mol. Phys., 6, 75.

12 ROWLINSON, J. S., 1963, Mol. Phys., 6, 429.

13 HIRSCHFELDER, J. O., CURTISS, C. F. and BIRD, R. B., 1954, Molecular Theory of Gases and Liquids (New York: John Wiley), Tables I-A, I-B and I-C.

14 BOYS, S. F. and SHAVITT, I., 1960, Proc. Roy. Soc. A, 254, 487.

15 BARKER, J. A. and MONAGHAN, J. J., 1962, J. Chem. Phys., 36, 2564.

16 BROWN, W. B. and ROWLINSON, J. S., 1960, Mol. Phys. 3, 35; ROWLINSON, J. S., 1960, ibid., 3, 265.

17 ALDER, B. J. and WAINWRIGHT, T. E. 1960, J. Chem. Phys., 33, 1439.

18 KIHARA, T. and HIKITA, T., 1953, Fourth Symposium on Combustion (Baltimore: Williams and Wilkins) p. 458.

19 FICKETT, W., WOOD, W. W., SALSBURG, Z. W., 1957, J. Chem. Phys., 27, 1324.

20 WOOD, W. W. and PARKER, F. R., quoted by FICKETT, W. and WOOD, W. W., 1960, Phys. Fluids, 3, 204.

21 KIHARA, T., 1958, Advances in Chemical Physics, 1, 267.

22 **WIEBE**, R., **GADDY**, V. L. and **HEINS**, C., 1931, J. Amer. Chem. Soc., <u>53</u>, 1721.

23 **MICHELS**, A., **DE GRAAFF**, W., **WASSENAAR**, T., and **LEVELT**, J. M. H., 1959, Physica, <u>25</u>, 25; **MICHELS**, A., **WASSENAAR**, T., and **LOUWERSE**, P., 1960, Physica, <u>26</u>, 539.

24 **WACKERLE**, J. D. and **HUGHES**, D. S., quoted in **FICKETT**, W., 1962, <u>Los Alamos Scientific Laboratory</u>, Report LA-2665.

25 **AMDUR**, I. and **MASON**, E. A., 1954, J. Chem. Phys., <u>22</u>, 670.

Legends for Figures

Figure 1	(no legend)
Figure 2	The calculated and exact second virial coefficient for $n = 12$.
Figure 3	The calculated and exact third virial coefficient for $n = 12$.
Figure 4	The fourth virial coefficient calculated from (4.1) and the values computed by Boys and Shavitt (circles) and by Barker and Monaghan (arrows) for $n = 12$.
Figure 5	The reduced pressure as a function of the density ξ for $n = \infty$. The full curves are the machine calculations of Alder and Wainwright. The dashed curves are discussed in the text. The vertical line is at the density of closest packing.
Figure 6	The calculated compression factors at $\tau = 20$ and $\tau = 100$ for $n = 12$. The points are the Monte Carlo calculations of Wood and Parker.
Figure 7	The compression factor of helium. The full curves are experimental and the dashed curves are calculated.
Figure 8	The compression factors of neon and hydrogen at 150°C. The full curves are experimental and the dashed curves are calculated.
Figure 9	The Hugoniot curves for argon for the potentials (5.7) and (5.8). The experimental points of Wackerle and Hughes are shown with their estimates of the experimental error.

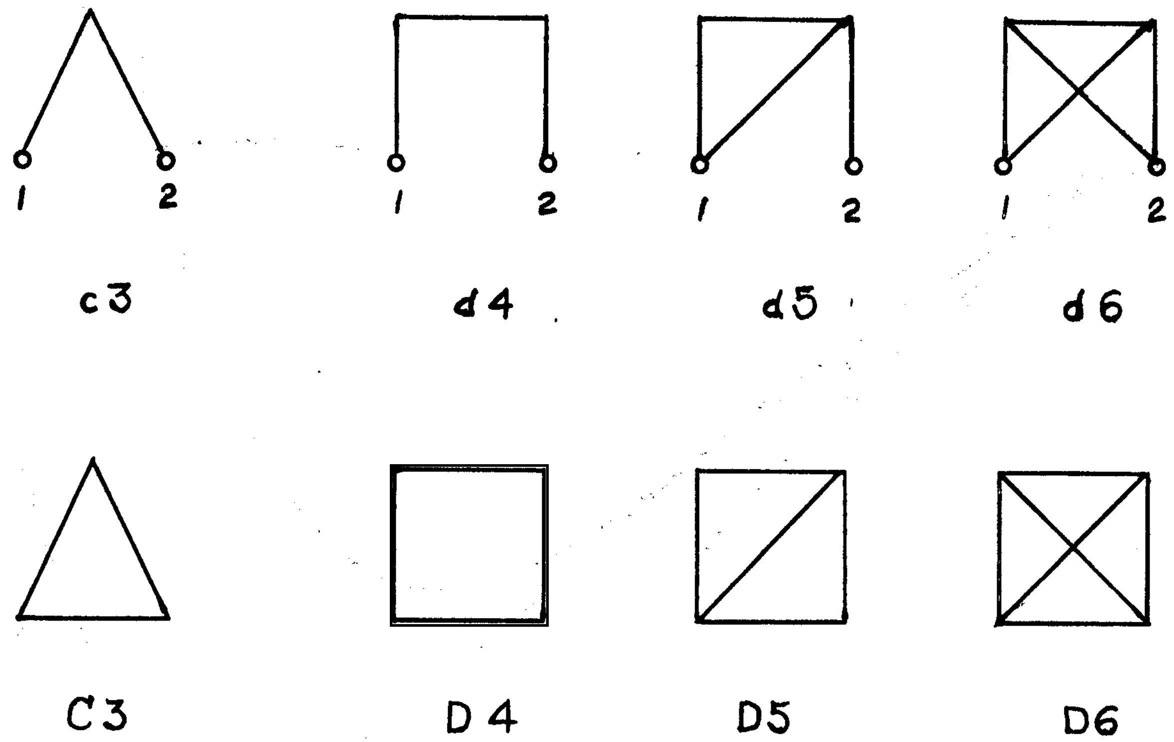

FIGURE 1

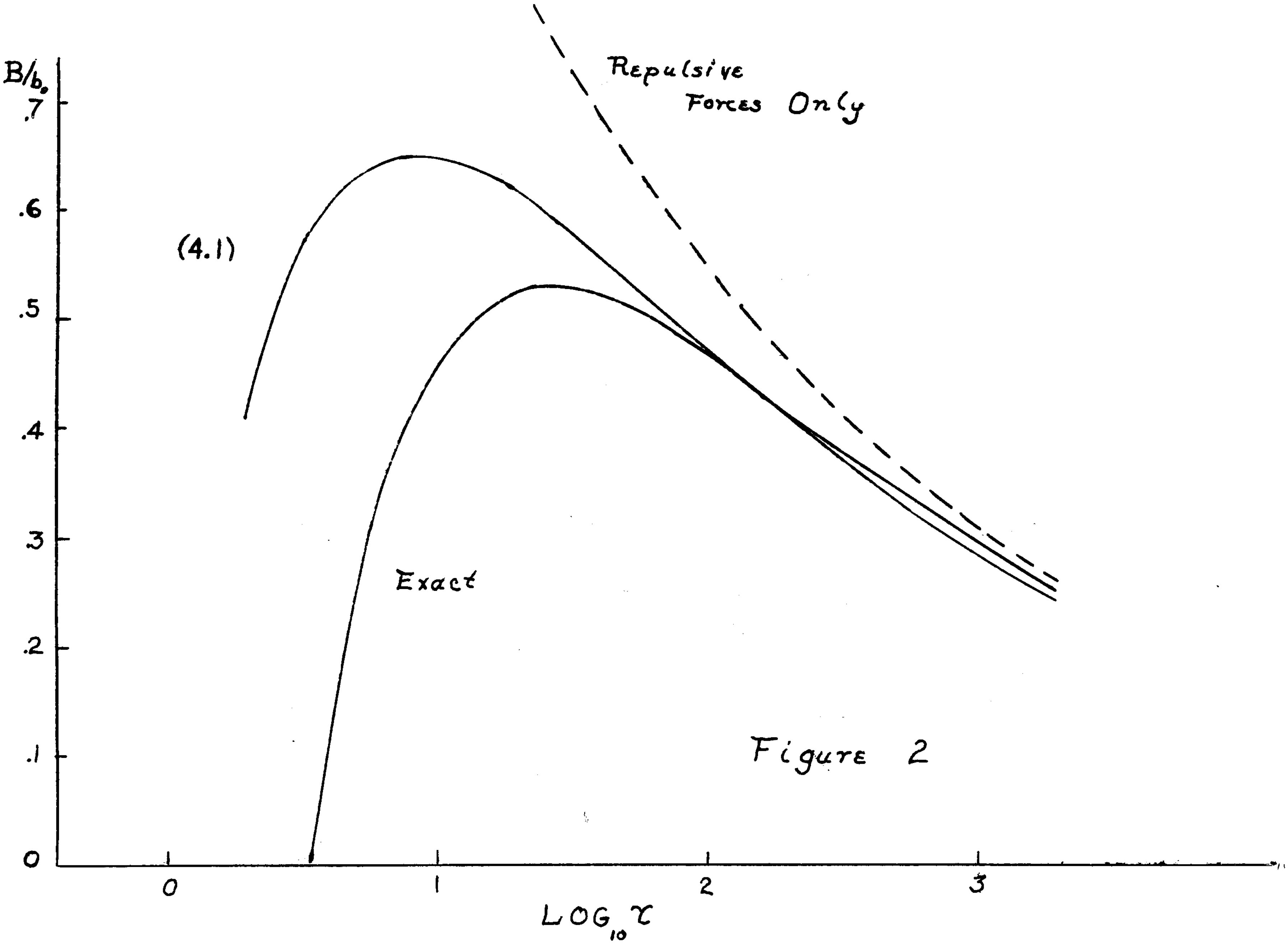

Figure 2

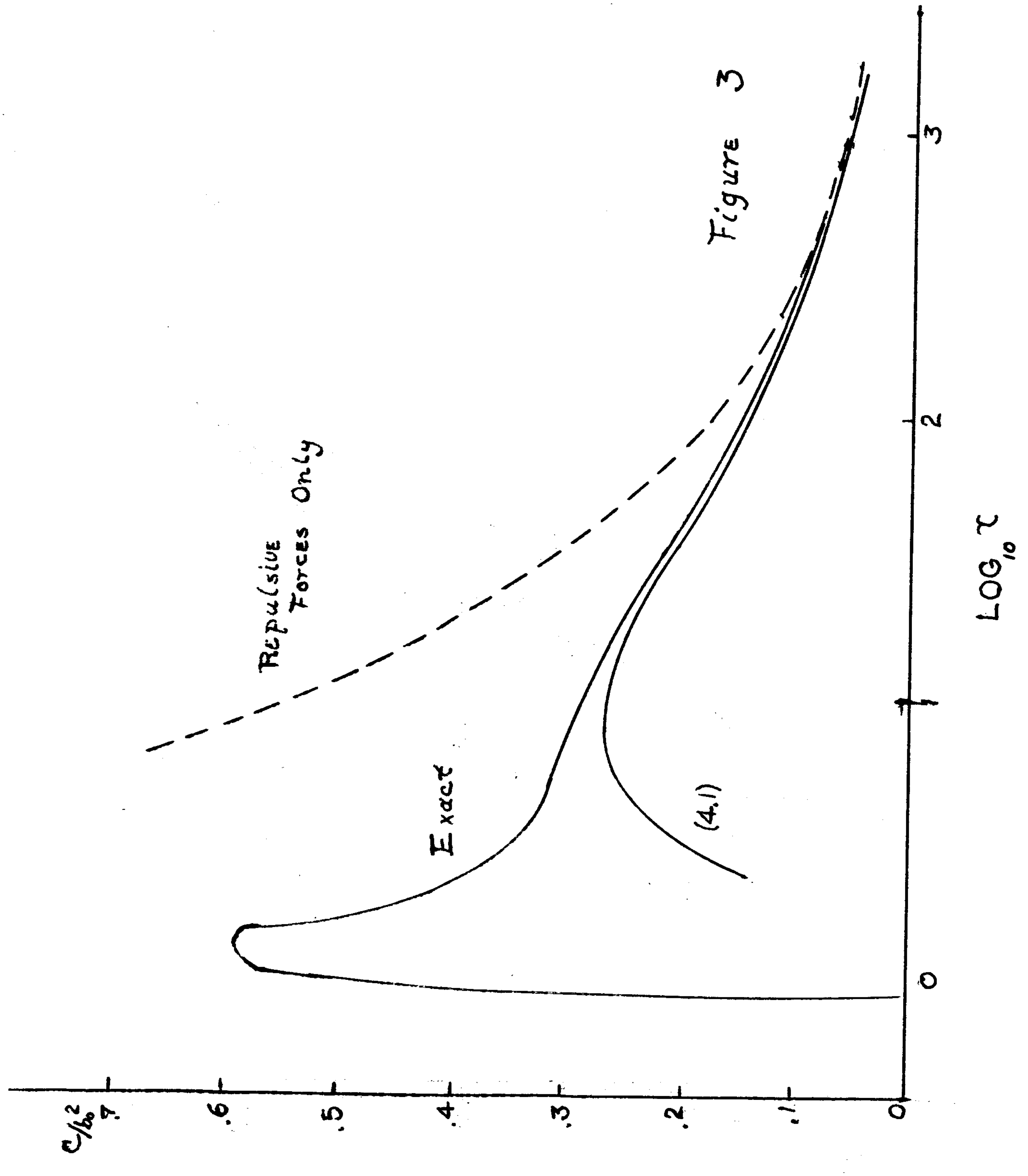
C/b_0^2
.7
.6
.5
.4
.3
.2
.1
0
0
1
2
3
$\mathrm{LOG}_{10}\,\tau$
Repulsive Forces Only
Exact
(4.1)

Figure 3

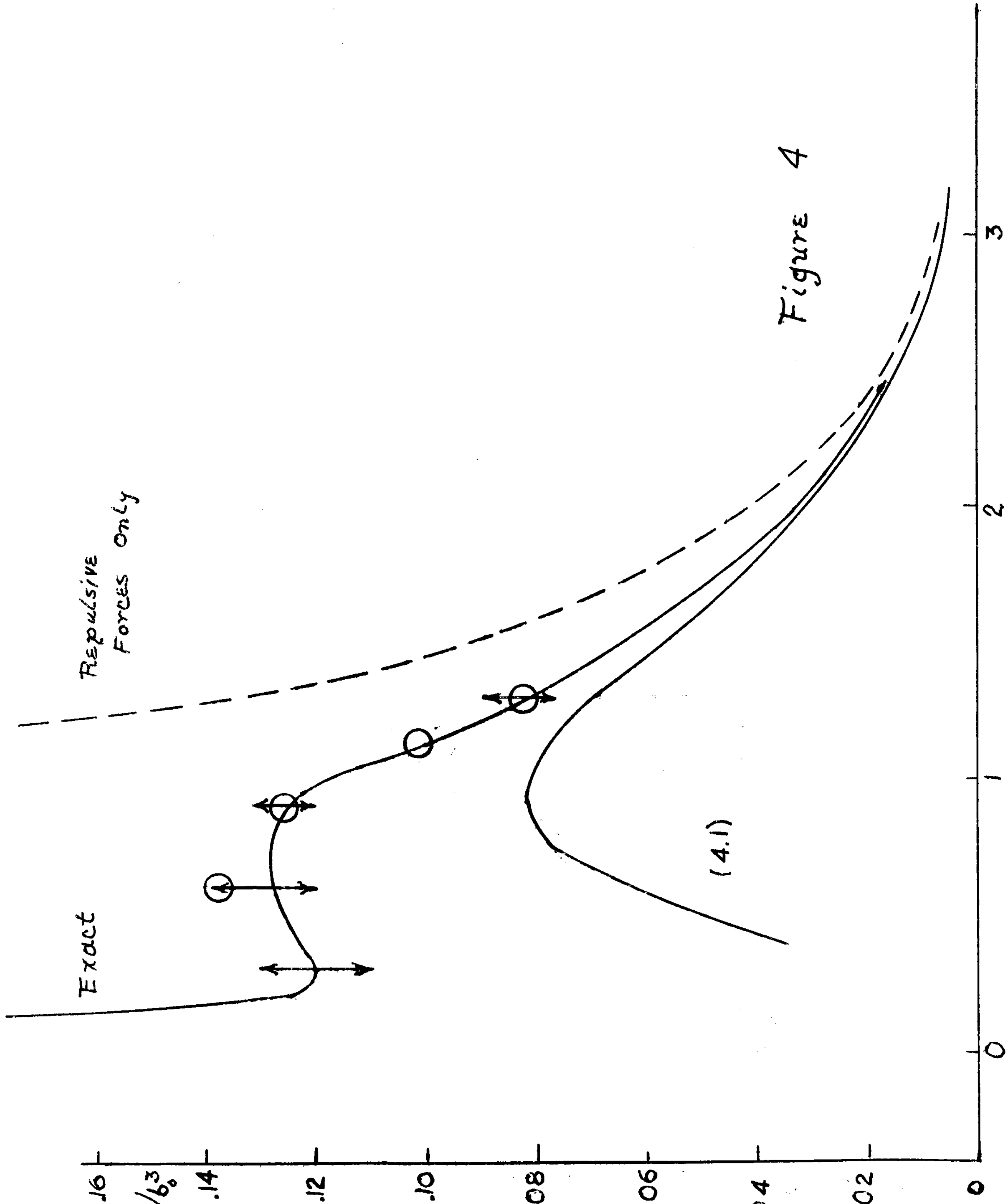
.16
D/σ_0^3
.14
.12
.10
.08
.06
.04
.02
0
0
1
2
3
$LOG_{10}\ \tau$
Exact
Repulsive Forces only
(4.1)

Figure 4

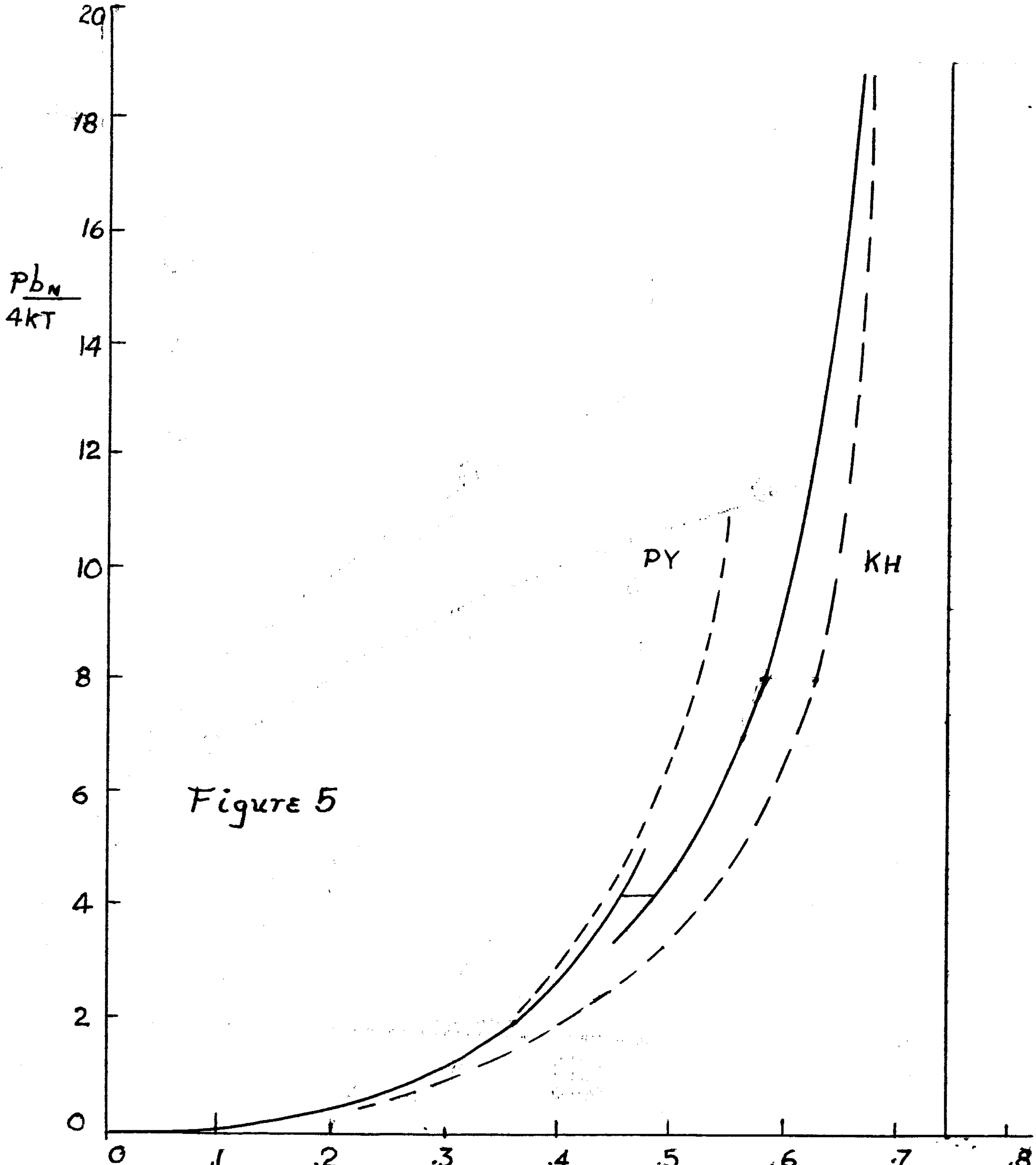

Figure 5

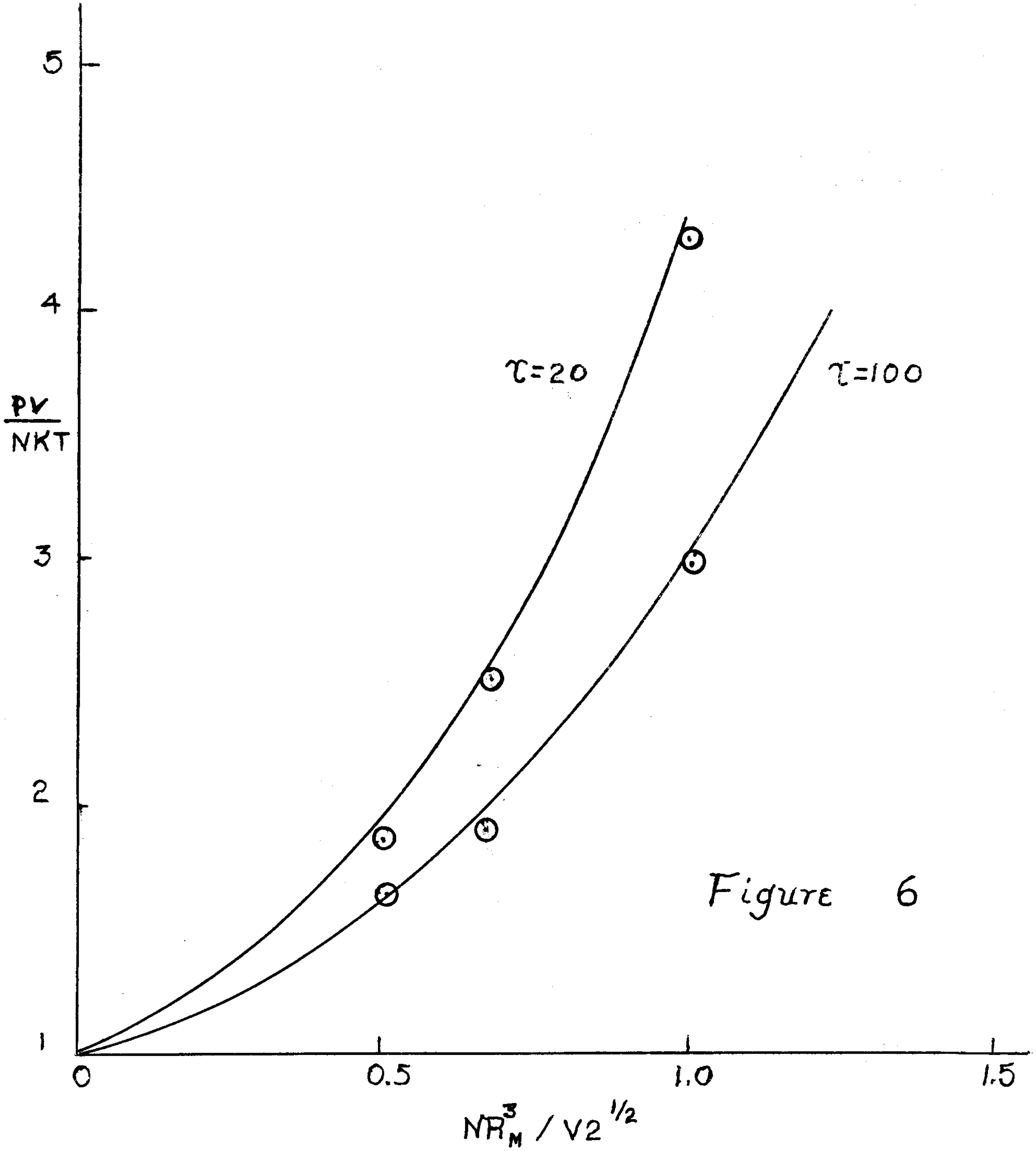

Figure 6

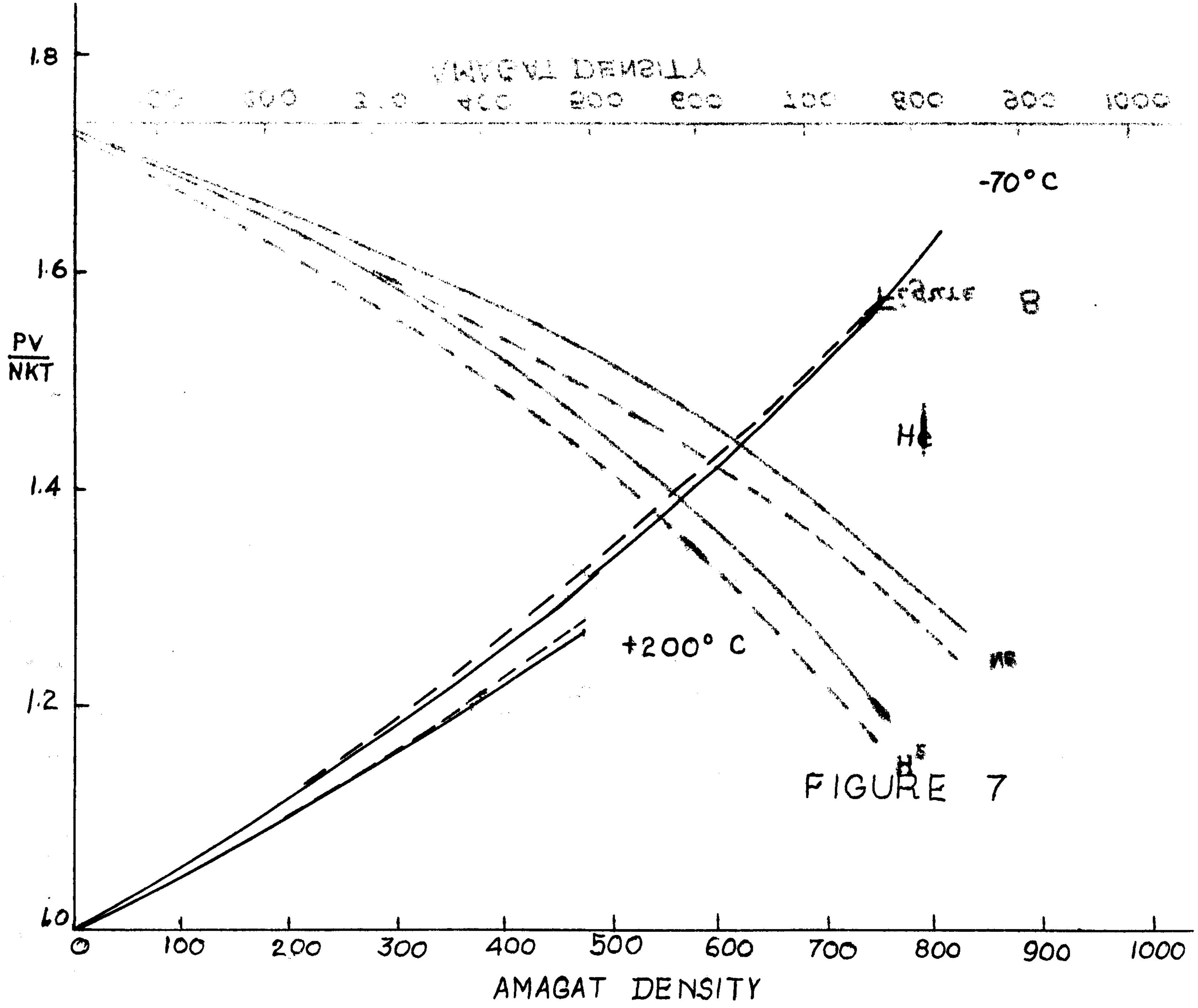
1.8
1.6
PV/NKT
1.4
1.2
1.0
0
100
200
300
400
500
600
700
800
900
1000
AMAGAT DENSITY
-70° C
+200° C

FIGURE 7

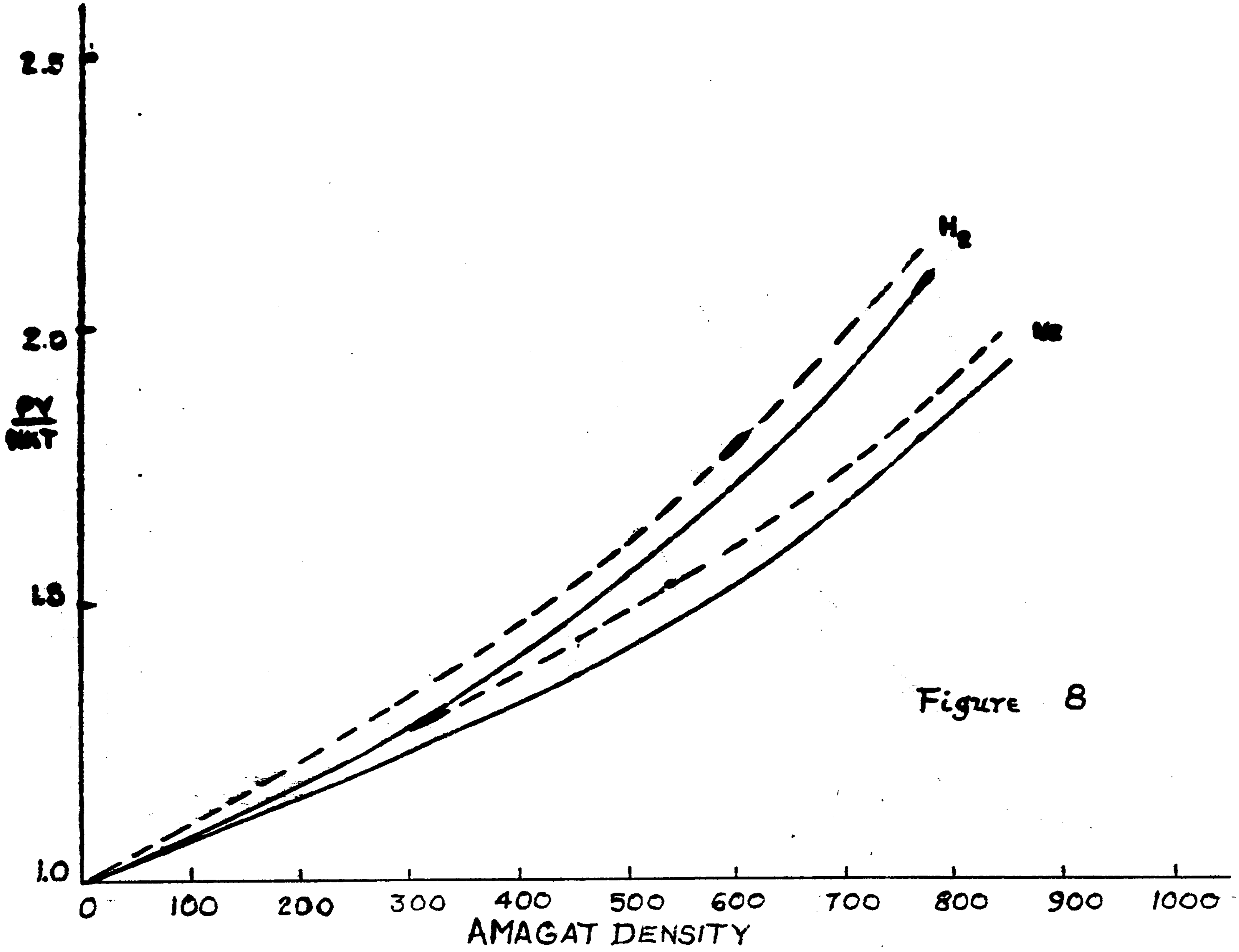
2.5
2.0
$\frac{PV}{NkT}$
1.5
1.0
0
100
200
300
400
500
600
700
800
900
1000
AMAGAT DENSITY
H_2
Ne

Figure 8

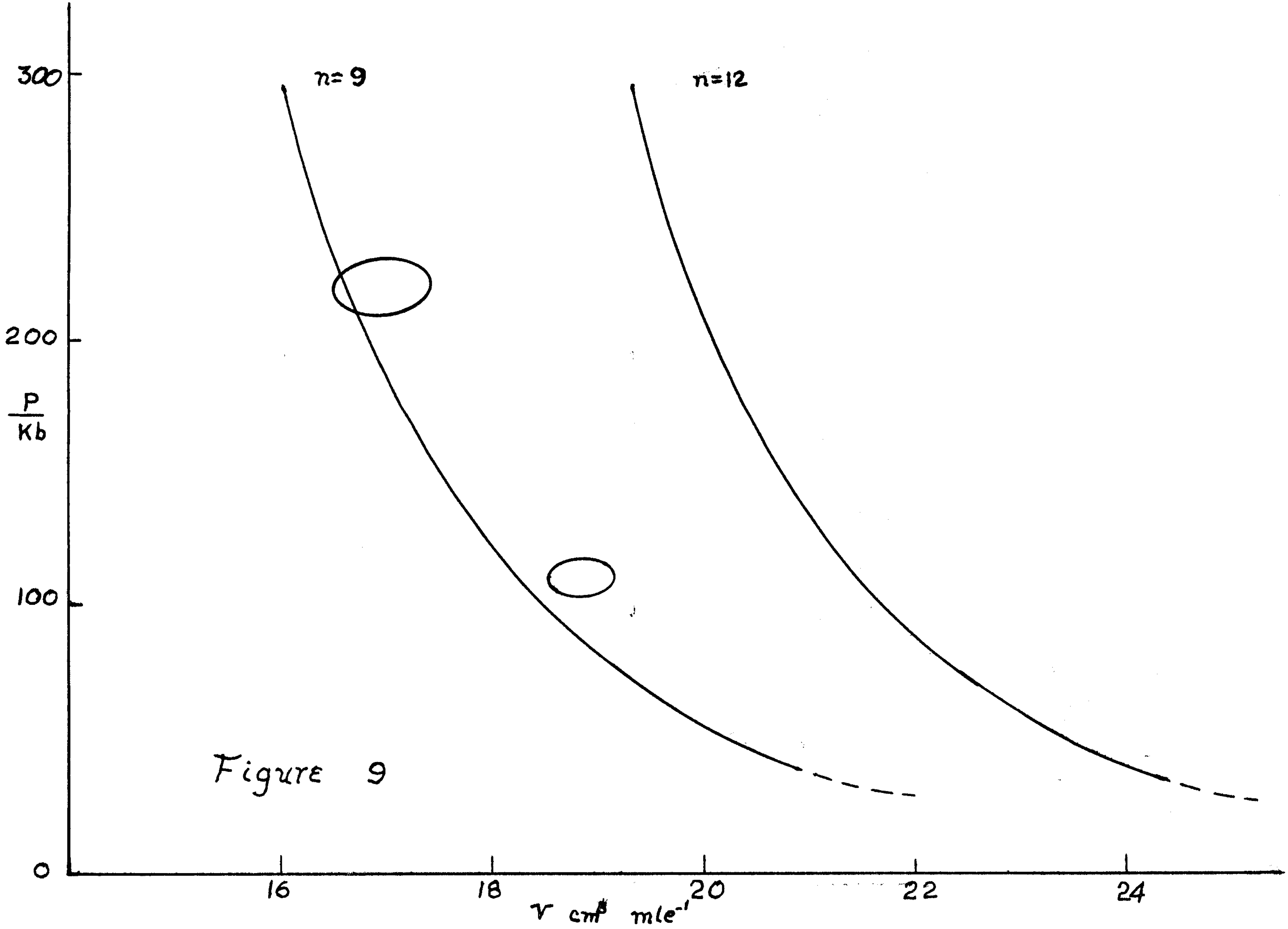

Figure 9