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Equation of State for Dense Gases*

LESTER HAAR AND STEPHEN H. SHENKER†

Institute for Basic Standards, National Bureau of Standards, Washington, D. C. 20234

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A simple quantitative equation of state of the van der Waals type is proposed for dense fluids. The equation yields compressibility factors with a precision comparable to those from the more complicated temperature perturbation theory when tested against "computer experiments", including isotherms as low as 0.8 liquid-vapor critical temperature. The equation is capable of predicting compressibility factors for real gases as illustrated by calculations for argon and nitrogen at pressures up to 10 000 atm. The derivation of the equation is based on a rearrangement of the terms in the Ursell–Mayer density expansion of the configuration integral. The equation contains two temperature-dependent parameters, to be determined from the dilute gas second virial coefficients. A principal feature of our approach is that it does not require explicit knowledge of the details of the pair interaction.

I. INTRODUCTION

A major objective of statistical mechanics is to predict the properties for real fluids at high densities from the known properties of the dilute gas. To accomplish this, it is usual practice to reduce known dilute gas properties to appropriate pair potentials for the molecular interactions. The properties of the dense fluid are then formulated in terms of the detailed structure of these pair potentials. Considerable progress has been realized using this approach. Noteworthy are the expansions in density based on Percus–Yevick (PY) theory[1] and expansions in reciprocal temperature using the Zwanzig theory[2] as modified by Barker and Henderson[3] (ZBH). The range of applications for these include several models for the pair potential, such as the hard and soft spheres, the square well, and the Lennard-Jones potential. The ZBH temperature perturbation theory[4a] appears to be the more successful when compared to results of computer experiments, particularly at liquid temperatures[4b] but also at high densities.

Though the ZBH theory is a physically satisfying approach and does compare well (except at low liquid temperatures) with results of "computer experiments," we note several practical limitations. The most serious of these is associated with the application of the theory to real fluids. In the ZBH theory the perturbation terms are obtained as an expansion about the hard sphere. Barker and Henderson have shown[3] that the theory can yield quantitative results when the sphere diameter is expressed in terms of a kind of Boltzmann average of the molecular separation, where the average is taken over the positive energy region of the pair potential. It is a fact, however, that the shape of the pair potential even for simple systems is quite uncertain.[5,6] In this connection it has been proven[7] that for realistic (nonmonotone) potentials it is not possible to obtain an unambiguous representation of the pair potential from second virial coefficients. Also at high densities the sphere volume tends to affect the equation-of-state properties somewhat like an excluded volume, so that ambiguities in the sphere diameter are amplified in their effect on the equation of state at high densities. Thus, though the theory is theoretically satisfying, its application would seem to be limited to situations where the pair potential is known, as is the case for "computer experiments." A second limitation is that to use this equation of state requires a complicated numerical integration. Because of this, results have so far been obtained as a theoretical end in themselves and are therefore of somewhat limited utility to the engineer or scientist who desires a simple analytic representation of the equation of state as a predictive tool.

In this paper we derive a quantitative equation of state for dense, real fluids which is much simpler than the ZBH temperature perturbation theory and furthermore does not require reference to the precise details of the pair potentials. The derivation is based on an expansion in density, where the reference state is a gas of hard spheres. It is argued that when the sphere diameter is chosen appropriately, the terms that account for the difference between the properties of the

real fluid and one of hard spheres are sharply attenuated at temperatures above the liquid-vapor critical, for densities up to that of the solid. It is shown that the temperature dependence of the equation of state at temperatures above the critical is determined from the numerical values of no more than "two integrals of state." (The two integrals we use are the second virial coefficient and its first temperature derivative.) In a previous paper[8] this general approach was employed to obtain the equation of state at high temperatures.

The theoretical development of the equation of state is given in Sec. II. In Sec. III comparisons are made with results of "computer experiments" and ZBH and other theories, as well as with experimental data for the real fluids nitrogen and argon. The results are discussed in Sec. IV.

II. DERIVATION OF THE EQUATION OF STATE

A derivation of the equation is based on the assumption that the N-body potential of the fluid can be represented by a sum of pair potentials and that the Ursell–Mayer[9] virial expansion in the density is valid. The virial series is transformed into a rapidly convergent expansion about the hard-sphere limit. Finally, the equations' parameters are fixed by imposing as boundary conditions the results of dilute gas theory.

The Ursell–Mayer expansion for the equation of state is written

$$Z=\sum_{n=1} B_n\rho^{n-1}, \tag{1}$$

where Z is the compressibility factor, defined by $Z=P\beta/\rho N$; ρ is the reciprocal volume, P is the pressure, $\beta=1/kT$, and N is the number of molecules in the system. The B_n are the virial coefficients: that is $B_1\equiv 1$; B_2, B_3, B_4, etc., are well-defined integrals involving the interactions between 2, 3, 4, etc., molecules. We now formally develop the virials about some arbitrary hard sphere via the identity

$$B_n\equiv B_n^{\rm hs}+B_n-B_n^{\rm hs}, \tag{2}$$

where $B_n^{\rm hs}$ is the nth virial coefficient for the hard sphere and rewrite Eq. (1),

$$Z=\sum_{n=1} B_n^{\rm hs}\rho^{n-1}+\sum_{n=1}(B_n-B_n^{\rm hs})\rho^{n-1}, \tag{3}$$

where, consistent with the formulation, $B_1^{\rm hs}=B_1=1$. The first sum on the right-hand side of Eq. (3) is the equation of state that would be obtained for a gas of identical hard spheres. The hard-sphere gas has been studied extensively both "experimentally" via molecular dynamics and Monte Carlo calculations and theoretically via PY theory, so that the hard-sphere summation is known for any particular sphere size. The task, therefore, is to obtain a simple representation for the perturbation terms, the second sum on the right of Eq. (3).

We present an argument that the perturbation terms, the second sum on the right-hand side in Eq. (3), converges rapidly, so that except at temperatures below the gas–liquid critical, only the term linear in density need be considered. It is intuitively clear that this convergence occurs at high temperatures.[10] The prospect that this convergence might persist to somewhat lower temperatures is implied in work by Woolley.[11]

To illustrate our argument, in Fig. 1 we plot a few of the lower virials for the Lennard-Jones 6–12 pair potential. The reduced virials B_2^*, B_3^*,[12] and B_4^* [13] with

$$B_n^*=B_n/(\tfrac{2}{3}\pi N\sigma^3)^{n-1}, \tag{4}$$

are plotted against the reduced temperature $T^*=(\beta\epsilon)^{-1}$, where σ is the Lennard-Jones length parameter and ϵ the well depth. At low temperatures the contribution from the attractive part of the potential (regions of negative energy) is important and the lower virials tend to large negative values, whereas at the higher temperatures the repulsive part of the potential (regions of positive energy) tends to yield the dominant contribution. Thus, in Fig. 1 we see that B_2^* monotonically increases from large negative values to positive, but with decreasing slope and finally passes through a maximum. It is apparent that as the temperature increases, the contribution of attraction decreases relative to that of repulsion, even though the contribution of repulsion is itself slowly decreasing with temperature. We suggest that at some temperature not much beyond the temperature where B_2^* achieves its maximum, the contribution of attraction is relatively small. This occurs at a reduced temperature somewhat above $T^*=30$. Thus if the hard-sphere contribution is chosen appropriately, we would expect that the perturbation terms *linear* in density would be small at temperatures somewhat above $T^*=30$. Likewise we expect that for the third, fourth, etc., virials, the contribution of attraction

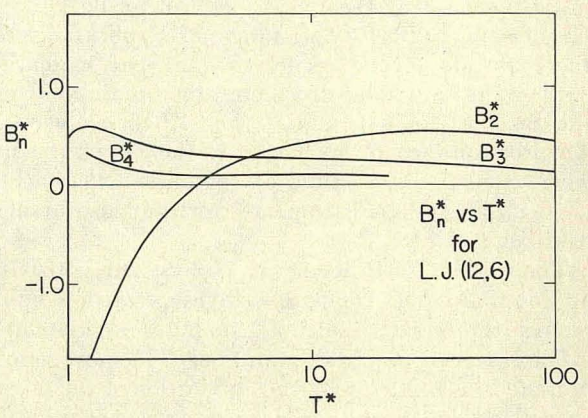

FIG. 1. Reduced virial coefficients B_n^* vs reduced temperature T^*. The maxima tend to lower temperatures with increasing n, supporting the argument in the text that except at low liquid temperature the higher virials are representable by hard-sphere interactions.

becomes relatively small at temperatures starting somewhat above the temperatures for which these virial coefficients achieve their (initial) maxima.[14] The maximum for the third virial occurs at about $T^*=1.25$ corresponding for simple substances to a temperature near the liquid–vapor critical. The temperature at which the fourth virial would achieve its maximum is in this neighborhood. (This is also true for the fifth virial[15] not shown in this figure.) We assume that this property of the virials is a general feature for any simple gas. Thus, we suggest that at temperatures above the critical the second virial coefficient includes the major effects due to molecular attractions, and that the higher virial coefficients are primarily determined by the repulsive interaction. We represent at any given temperature the repulsion between the molecules by that of a gas of identical hard spheres of size appropriate to that temperature.

Based on these arguments the equation of state [Eq. (3)] for a fluid at temperatures above the liquid–vapor critical can be truncated after the linear term in the attractive contribution. To represent the hard-sphere gas we employ the results of Percus–Yevick theory using the compressibility form for the equation of state.[16] This is a good approximation at low densities and is only in error by about 5% at densities approaching $\frac{2}{3}$ close packing of hard spheres.[17] Thus the equation of state is written

$$Z\cong[(1+y+y^2)/(1-y)^3]+4y[(B_2/b)-1], \qquad (5)$$

where $4y=b\rho$, and b is the hard-sphere second virial coefficient,

$$b=\tfrac{2}{3}\pi N a^3. \qquad (6)$$

The quantity $a(T)$ is the sphere diameter, which, in accord with the derivation, is temperature dependent. It is apparent that for a given temperature, Eq. (5) is a two-constant equation of state. Another feature is that the equation is easily integrable in closed form to yield a free energy.

The evaluation of the two equation-of-state parameters requires two boundary conditions at each temperature, and for this purpose we employ the numerical values for the second virial coefficient and its first temperature derivative. Thus we require at the threshold of zero density that the density dependence of the compressibility factor and the internal energy as obtained with Eq. (5) agree with theory for dilute gases. To utilize these boundary conditions we introduce an effective interaction that has the general features of a pair potential, except it is characterized by a hard-sphere cutoff at some diameter $a(T)$. This is joined to an attractive bowl of well depth $\epsilon(T)$. We consider a class of such functions obtained by joining the hard sphere at zero energy to a (6-m) Lennard-Jones bowl, where m is a characteristic constant for the fluid. These functions, which we shall refer to as

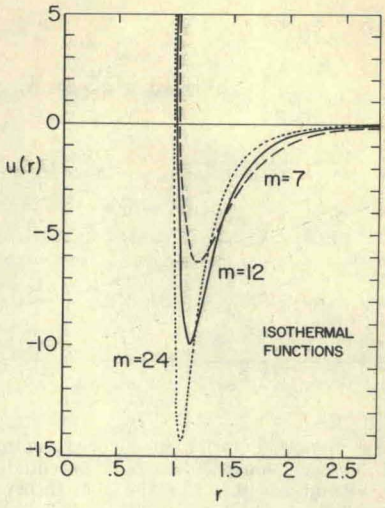

FIG. 2. Isothermal functions, Eq. (7), vs molecular separation in arbitrary units for a Lennard-Jones 6–12 potential at $T^*=2.5$. It is seen that though the shape of the "bowl" is quite sensitive to the characteristic parameter m, the sphere diameter at this temperature is only weakly sensitive.

isothermal functions, are written

$$u=p\epsilon[(a/r)^m-(a/r)^6], \qquad r>a$$
$$u=\infty, \qquad r<a, \qquad (7)$$

where $p\equiv[k/(k-1)]k^{(k-1)^{-1}}$ and $6k=m$, $m>6$. The first boundary condition yields the equation,

$$B_2=2\pi N\int_0^\infty r^2(1-e^{-\beta u})\,dr, \qquad (8)$$

where B_2 is the experimental second virial coefficient. Equation (8) is easily integrated with the result

$$B_2/b=1-\sum_{n=1} C_n(p\beta\epsilon)^n, \qquad (9)$$

where

$$C_n=\sum_{l=0}^{n}\frac{(-)^l}{l!(n-l)!}\{2[n+l(k-1)]-1\}^{-1}.$$

The second boundary condition is obtained by taking the temperature derivative of Eq. (9),

$$dB_2/dT=(d/dT)b[1-\sum_{n=1} C_n(p\beta\epsilon)^n]. \qquad (10)$$

Equations (9) and (10) are two equations in the two unknowns $a(T)$ and $\epsilon(T)$. The solution is simplified by assuming that $a(T)$ and $\epsilon(T)$ are slowly varying functions of temperature. The calculated $a(T)$ value together with the value of the second virial coefficient are then employed as the two parameters in Eq. (5) for evaluation of the equation of state along that isotherm.

We now investigate the sensitivity of the equation of state, Eq. (5), to the characteristic fluid constant m. In Fig. 2 several 6-m isothermal functions defined

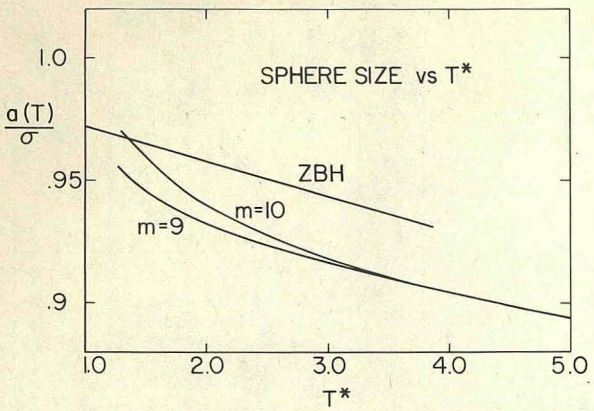

FIG. 3. The sphere diameter in reduced units vs reduced temperature for the Lennard-Jones 6–12 potential. Results are shown for $m=9$ and $m=10$ and for the ZBH theory.

by Eq. (7) are shown. The parameters a and ϵ for these isothermal functions were calculated from Eqs. (9) and (10) using the values for B_2 and dB_2/dT that correspond to a Lennard-Jones 6–12 potential at a reduced temperature $T^*=2.5$. The scale of the abscissa is normalized so that $a(T)=1$ for the isothermal function given by $m=12$. At this temperature $a(T)$ and, hence, the equation of state is relatively insensitive to the shape of the bowl, that is to m. In fact, at high temperatures the sphere diameter is independent of the shape of the bowl. (For these situations the evaluation of the sphere size is further simplified, as will be discussed at the end of this section.) As the temperature is reduced, the hard-sphere size tends to be increasingly sensitive to m. To determine the value for m, the equation-of-state calculations for various values for m should be compared with experimental PVT data at a low temperature and at densities in the neighborhood of twice the critical. In this paper we make this "fit" for an isotherm near $\frac{3}{2}$ the critical temperature.

It is easily determined that $m=9$ and $m=10$, respectively, are fair estimates for argon and molecular nitrogen, the two real fluids considered in this paper. (However, since the sensitivity of the equation-of-state properties to m is weak except at low temperatures, if the temperature of interest does not extend much below twice the critical, $m=9$ could also be used for nitrogen.) We also use $m=9$ for the Lennard-Jones fluid to compare our theory with "computer experiments" and temperature perturbation theory.

In Fig. 3 a plot of the sphere diameter $a(T)$ vs T^* is shown for the two isothermal functions corresponding to $m=9$ and $m=10$. The Lennard-Jones 6–12 potential was again used to generate B_2 and dB_2/dT values. In this figure we show also the sphere diameter as reported for ZBH perturbation theory.[3] As expected, the sphere diameter is a monotone decreasing function of the temperature. It should be appreciated that the hard-sphere diameters are convenient artifices. Physical interpretation is meaningful only in the context of the particular over-all theory. However, since the ZBH and the present theory are quite sensitive to the hard-sphere diameter, agreement to within several percent for $a(T)$ would be necessary if the two approaches are to yield comparable equation-of-state properties at high densities.

The choice of a particular isothermal function, that is the shape of the potential bowl in Eqs. (7), is far from unique, for in addition to the dependence on m,

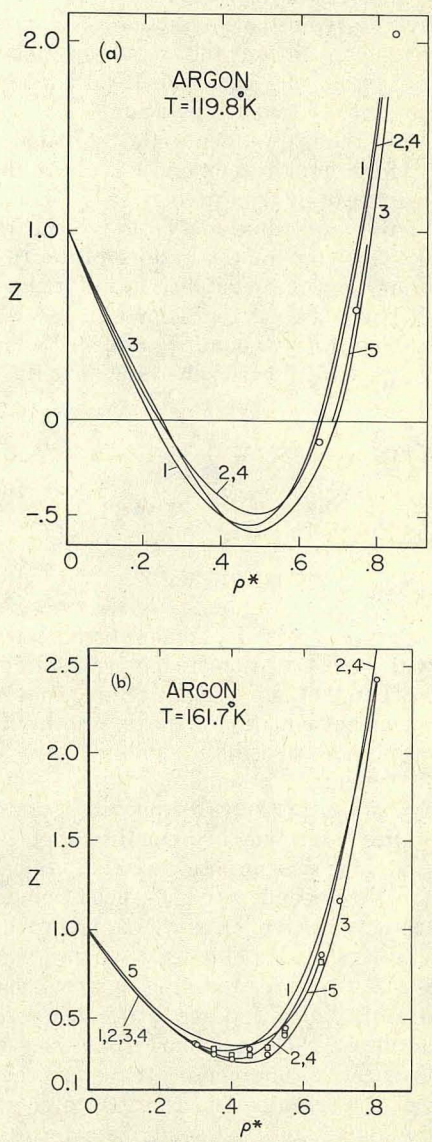

FIG. 4. Compressibility factor for argon vs reduced density $\rho(N\sigma^3)\equiv\rho^*$. Curves 1, this work; Curves 2 and 4, ZBH theory from references 20 and 22, respectively; Curves 3, ZBH theory based on Monte Carlo calculation of perturbation terms[21]; Curves 5, PVT exptl data.[19,23,24] The "computer experiments"[25,26] are designated by circles, Monte Carlo; and squares, molecular dynamics.

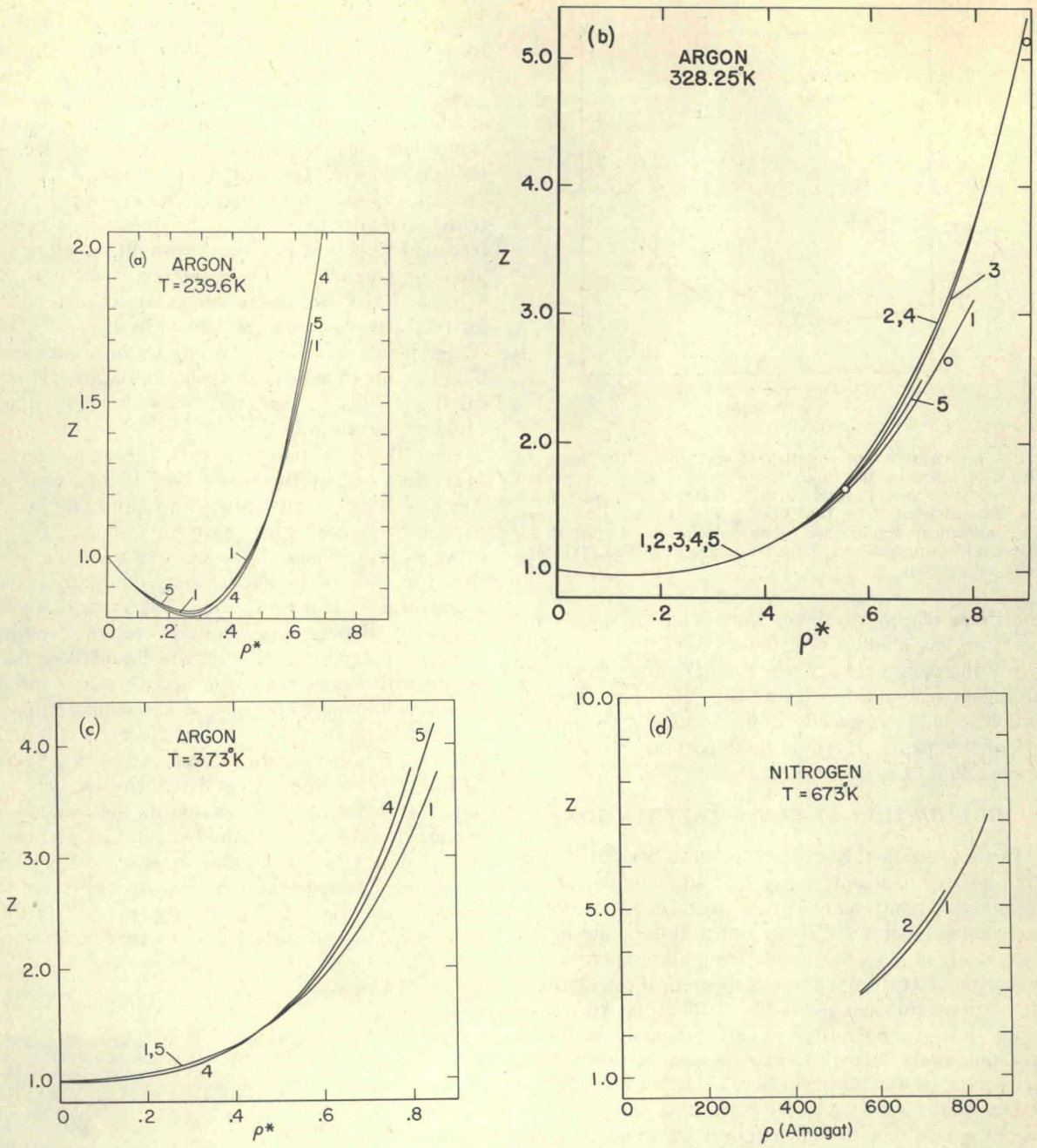

FIG. 5. Compressibility factor vs density for argon; see caption, Fig. 4.

the bowl shape could be affected by adjusting the exponent in the *attractive* term. In fact the sphere sizes (the curves labeled $m=9$ and $m=10$) shown in Fig. 3 could each be approximated by any of a class of "m-n" isothermal functions. Such redundance, of course, renders the task of determining the isothermal function that much simpler. It suggests that the equation of state is a relatively insensitive probe of the pair potential even at the higher densities.

The equation of state derived in this section is, in principle, limited to temperatures above the liquid–vapor critical. At lower temperatures the higher perturbation terms in the density expansion, Eq. (3), become important, so that additional attractive terms for Eq. (5) would appear to be needed. Also there is doubt as to the validity of the virial expansion, Eq. (1), for the liquid.[18] However, as will be seen in the next section, the equation of state can be extended somewhat into the liquid range, but with some deterioration in predictive accuracy.

At high temperatures, the theory is simplified by the fact that the hard-sphere diameter is insensitive to

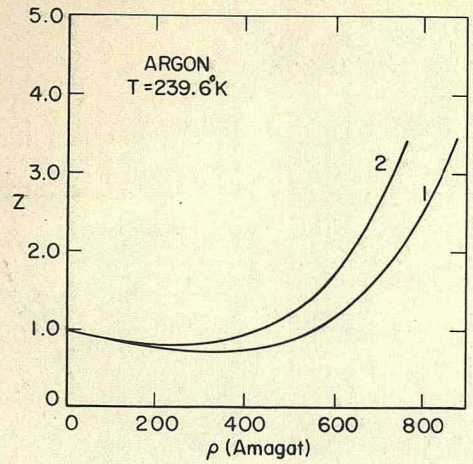

FIG. 6. Sensitivity of equation of state for ZBH theory to choice of potential function. Compressibility factor is plotted vs density in amagat. For Curve 1, the reference potential is the Lennard-Jones 6–18; for Curve 2, the Lennard-Jones 6–12. The numerical results are from calculations furnished by Toxvaerd[22] using potential parameters given by Eqs. (11) and (10), respectively.

the shape of the attractive bowl. Thus at some temperature, say about 3 or 4 times the critical, we could freeze the parameter $\epsilon(T)$ in Eqs. (7) and (9) and at all higher temperatures ignore Eq. (10). This simplification would have no effect on the calculations in Sec. III of this paper. It would be important, however, in applications at high temperatures.

III. EQUATION-OF-STATE CALCULATIONS

In this section the equation of state derived in Sec. II is used to calculate compressibility factors for the real fluids argon and molecular nitrogen. The results are compared with PVT experimental data and in the case of argon with results of "computer experiments" and with ZBH theory. For our theoretical calculations, the experimental second virial coefficients we use as input data are smoothed values obtained via model pair potentials "fitted" to experimental second virials. (However, as was shown in Sec. II, it is the numerical values of the second virials rather than the particular model potential with which they were smoothed that is required as input information for our theory.)

The Figs. 4 and 5 contain equation-of-state isotherms for argon. The compressibility factor is plotted vs the reduced density, $\rho^*=N\sigma^3\rho$, for isotherms from 119.8°K ($\simeq$0.8 critical) to 673.15°K. Curves labeled 1 present the compressibility factors predicted by our equation of state. To facilitate the calculation we represented the experimental second virial coefficients by an interpolation formula corresponding to the "6–12" pair potential with parameters,[19]

$$\epsilon/k=119.8°\text{K},\qquad \sigma=3.405\ \text{Å}. \tag{11}$$

The curves 2, 3, and 4 represent results of second-order temperature perturbation (ZBH) theory, for a Lennard-Jones gas with parameters, Eq. (11), as reported in Refs. 20–22, respectively. The curves 2 and 4 are obtained by numerical integration of approximate expressions for the perturbation terms and are essentially equivalent treatments. The curves 3 refer to an "exact" calculation of the second-order perturbation terms via Monte Carlo techniques. The curves 5 represent experimental compressibility factors measured for argon.[19,23,24] The data points on Figs. 4(a), 4(b), and 5(b) are results of "computer experiments" for the Lennard-Jones gas defined by Eq. (11),[25,26] the circled points referring to Monte Carlo results and the boxed points to molecular dynamics results. (It is indicated in Ref. 25 that the "computer experiments" could be uncertain by 5%–10%.)

Since the 6–12 potential with the parameters, Eq. (11), does not fit the second virials for argon below 200°K,[19] Figs. 4 are interesting primarily as comparisons of theory with the results of the "computer experiments". These figures show that the present theory as well as the ZBH is only qualitative at these temperatures. However, the ZBH curves 3 yield a somewhat closer approximation to the results of "computer experiments" for the liquid densities. In accord with the derivation in Sec. II, our equation-of-state results tend to degrade at low temperatures. But it is apparent from Figs. 4 the theory is still at least qualitative at temperatures even as low as 0.8 critical. In fact it is only for curves 3 (which involve a "computer experiment" to evaluate the second-order perturbation terms) that the temperature perturbation results are a significant improvement.

Figures 5 include the temperature region for which the 6–12 pair potential yields a good "fit" to the experimental second virial data, so that comparison of

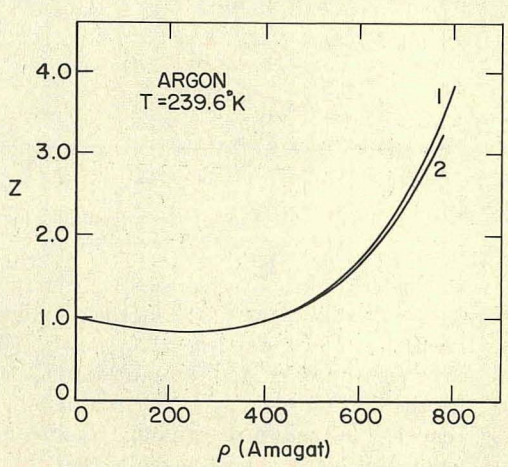

FIG. 7. Sensitivity of present theory to choice of potential functions. Potential functions are as described in caption for Fig. 6. The small difference between Curves 1 and 2 is mostly due to the slight differences in second virials produced by the two potentials in the vicinity of the isotherm.

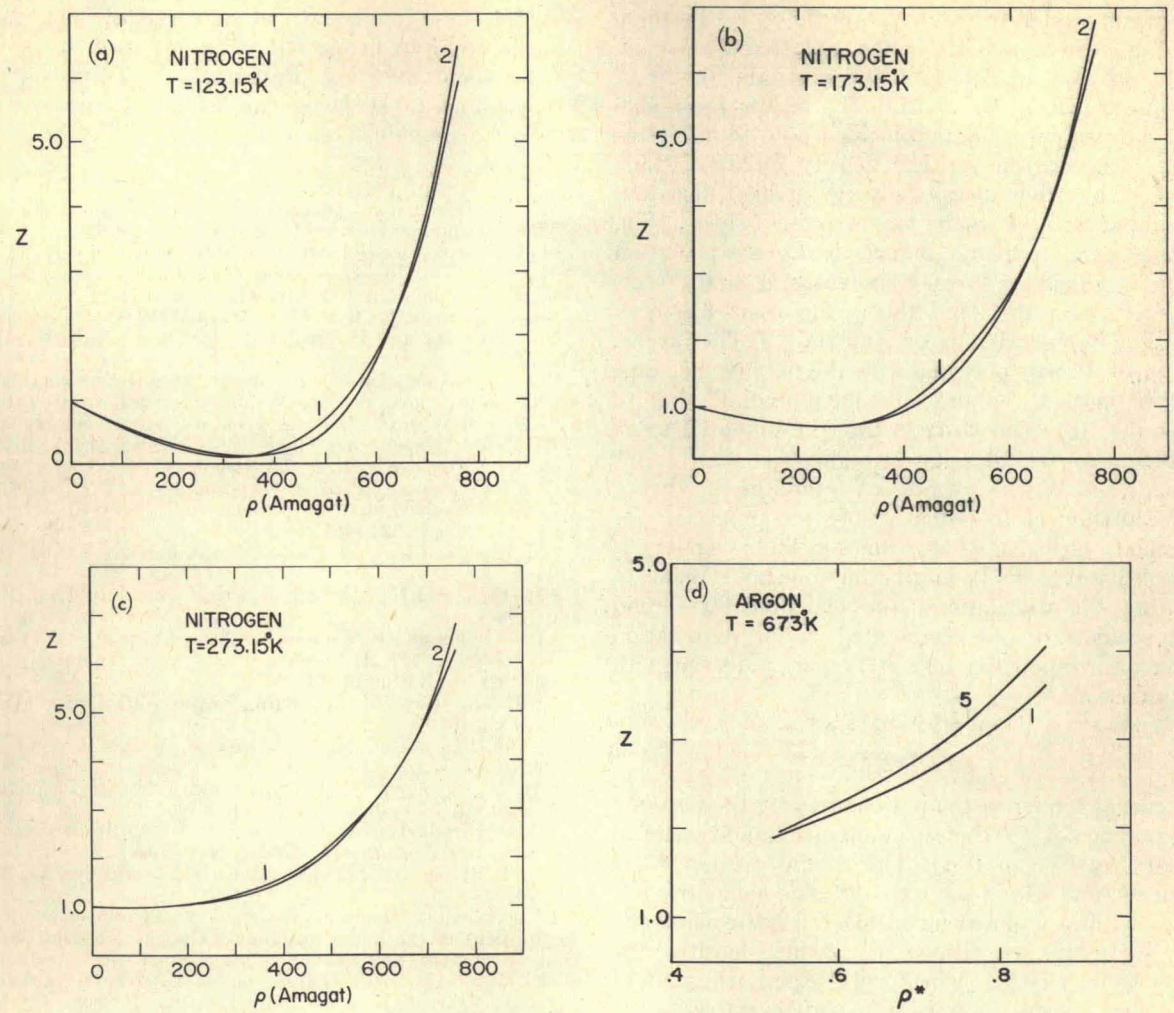

FIG. 8. Compressibility factor vs density in amagat for nitrogen. Curves 1, present theory; Curves 2, experimental PVT measurements.[30,31]

our results with the experimental PVT measurements for these temperatures is more meaningful. The present theory (curves 1) tends to follow the PVT experimental data (curves 5) fairly closely at the lower densities, up to about $\rho^*=0.6$ (approximately twice the critical density). At higher densities, the present theory tends to yield values that are low, but in most cases by less than 5%. The results are roughly comparable to those for the ZBH theory, however, the ZBH (curves 2–4) tend to underestimate at densities near the critical and to overestimate at high densities. The results of the "computer experiments" seem to scatter. Thus in Fig. 5(b) at $\rho^*=0.75$ the Monte Carlo results tend to favor the present theory, whereas at $\rho^*=0.9$, the ZBH; at $\rho^*=0.55$ they fall between the results of the two theories, almost on the PVT experimental curve 5.

It was stated in the Introduction that uncertainties in the pair potential for real fluids limit the utility of the ZBH theory as a tool for predicting equation-of-state properties for real fluids. To illustrate this we compare the equation of state of argon for a particular isotherm with the ZBH theory, using different inverse power representations for the pair potential. The same comparison is then made for the present theory. In the temperature range included in Figs. 5 a number of different shaped potentials could be employed which would yield adequate "fits" to the experimental second virials.[6] The "fit" for the 6–18 potential, for example, yields the parameters,[27]

$$\epsilon/k=160.87°\text{K} \quad (\text{"6–18" for argon, "best fit"}),$$
$$\sigma=3.261\ \text{Å}. \qquad (12)$$

We present in Figs. 6 and 7 the equation-of-state results for two representations for the pair potential for argon: the "6–18" with parameters given by Eqs. (12), curves 1; the 6–12 with parameters given by Eqs. (11), curves 2. Figure 6 includes the results for

the ZBH theory; Fig. 7 those of the present theory. Both figures refer to the isotherm 239.8°K. In these figures the compressibility factor is plotted against the density in amagat. All the numerical data for Fig. 6 were furnished by Toxvaerd.[22] The results for Fig. 6 show the two curves near coincidence up to a density about $\frac{2}{3}$ the critical (critical density for argon$\cong$300 amagat). But they sharply diverge at high densities. By comparison, the results for the present theory, Fig. 7, are relatively potential independent. An explanation for the fact that the "wrong" potential gives the "correct" results in the ZBH theory for argon has been offered by Barker, Henderson, and Smity.[28] They argue, that the 6–12 pair potential with the parameters, Eqs. (11), happens to be an "effective potential" that to first order for argon corrects the true potential so as to account for high density nonadditive effects.

Finally, in Figs. 8 we present results of the theory for calculation of the equation-of-state properties for molecular nitrogen. The compressibility factor is plotted vs the fluid density in amagat. Again to facilitate the calculations, the experimental second virial coefficients were represented by an interpolation formula corresponding to a 6–12 pair potential with parameters[29]

$$\epsilon/k = 95.781°\text{K},$$
$$\sigma = 3.712\ \text{Å}. \qquad (13)$$

The curves 1 refer to the present theory; the curves 2 to experimental PVT measurements[30,31] and extend to 10 000 atm in Fig. 8(d). The sphere diameters are obtained from Fig. 3 with $m=10$. The comparison of theory with experiment for nitrogen is quite similar to that for argon. As with argon, at low densities the theory is in good agreement with experiment, but at the higher densities the PVT experimental isotherms tend to be slightly steeper.

IV. DISCUSSION

In this paper we derived an equation of state for fluids without recourse to detailed information about the microscopic structure of the fluid. The derived equation has been employed in Sec. III to calculate the equation of state for the simple fluids argon and nitrogen. Comparison was made with thermodynamic measurements, with "computer experiments," and with temperature perturbation theory. It was shown that uncertainties in knowledge of the pair potential can seriously degrade the results of existing theories, such as temperature perturbation theory, a limitation not present with the theory presented here. It was shown that up to densities approaching the solid, our equation provides a means to predict equation-of-state properties for real fluids.

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† Present address: Harvard College, Cambridge, Mass.

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