

Linear Isotherms for Dense Fluids: A New Regularity

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A general regularity has been found for dense fluids, both compressed liquids and dense supercritical fluids, namely, that $(Z - 1)v^2$ varies linearly with respect to ρ^2 , where $Z \equiv pv/RT$ is the compression factor and $\rho = 1/v$ is the molar density. The regularity is tested with experimental data for 13 fluids (Ar, N₂, O₂, CO, CH₄, C₂H₆, C₃H₈, C₂H₄, C₂H₂, C₆H₆, CH₃OH, NH₃, H₂). It is shown to be compatible with equations of state based on statistical-mechanical theory, although the latter do not predict as great a range of linearity as is suggested by experiment. The regularity holds experimentally for densities greater than the Boyle density and for temperatures below about twice the Boyle temperature. The upper density limit is less certain but seems to be the freezing line for liquids ($T < T_c$) and at least about twice the Boyle density for supercritical fluids. The temperature dependences of the intercept and slope of the linearity are predicted from a simple model and are in good agreement with experiment.

Introduction

Liquids and dense fluids are usually considered to be complicated on a molecular scale, and a satisfactory theory of liquids only began to emerge in the 1960s.¹ However, they show a number of simple regularities, some of which have been known for years without any theoretical basis. We mention just three examples. The first is the Tait–Murnaghan relation, known for over 100 years, in which the bulk modulus (reciprocal compressibility) of a liquid (or solid) is linear in the pressure.² The second is the linear relation between temperature and density at unit compression factor ($Z \equiv pv/RT = 1$), discovered empirically in 1906, then forgotten and rediscovered several times, and recently christened the “Zeno line”.³ Both of these examples are quite old. The third example is much more recent: the common bulk modulus point, in which all the liquid isotherms of the reduced bulk modulus as a function of molar volume intersect at essentially a single point.⁴ Some of the known regularities have been given a theoretical basis, but others remain completely empirical.

The purpose of this paper is to point out a new regularity that applies both to compressed liquids and to dense supercritical fluids and to give some theoretical basis for this regularity. The regularity is that the quantity $(Z - 1)v^2$ is linear in ρ^2 , where $\rho = 1/v$ is the molar density. This relation was originally suggested on the basis of a simple lattice-type model applied to a Lennard-Jones (12,6) fluid.⁵ Here we first investigate the validity of the relation by examining experimental p – v – T data for a number of real fluids. We then show how the temperature dependences of the intercept and slope can be predicted from a simple model and compare the prediction with experimental results. Finally, we examine whether equations of state based on statistical-mechanical theory predict such a linear relation in the dense-fluid region.

Experimental Tests

In examining the linearity of $(Z - 1)v^2$ vs ρ^2 , we wish to address the following specific questions: (i) Over what range of density does the linearity hold for these isotherms? (ii) Over what temperature range does it hold? (iii) For what types of fluids is the linearity valid? (iv) Does $(Z - 1)v^2$ vary linearly only with ρ^2 ? How about ρ and ρ^3 ?

Argon and nitrogen serve as our primary test fluids because of the abundance of available p – v – T data. Such data are more limited for most of the other fluids examined.

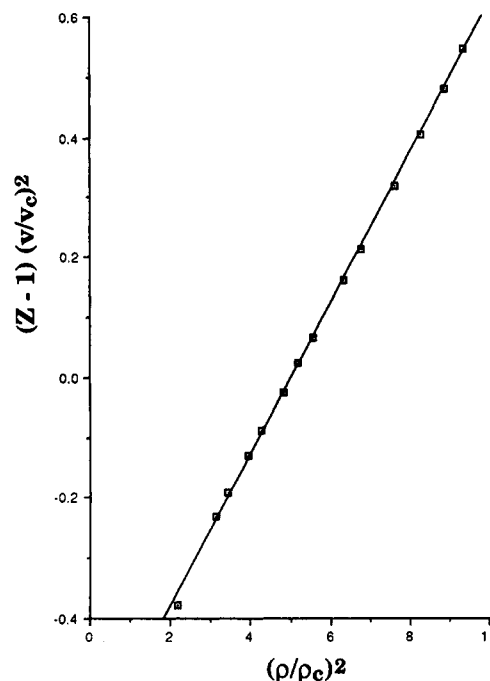


Figure 1. Typical isotherm of $(Z - 1)v^2$ vs ρ^2 for liquid Ar at 150 K.

We begin with Ar in its liquid range.⁶ (By liquid we mean $T < T_c$.) Except near the critical point, all the liquid isotherms are found to be quite linear over almost the entire density range from the vaporization line to the freezing line. A typical isotherm (150 K) is shown in Figure 1, where it can be seen that only the point at the lowest density deviates significantly from the linear relation. For convenience only, the molar densities and volumes have been reduced by the critical value⁶ $\rho_c = 13.29$ mol/L. It turns out that all the Ar(l) isotherms become linear for $\rho \gtrsim 23$ mol/L and that this is nearly equal to the Boyle density of about 24 mol/L. The Boyle temperature T_B and Boyle volume v_B are defined in terms of the second virial coefficient B_2 as follows: $B_2(T_B) = 0$ and $v_B = T_B B_2'(T_B)$, where $B_2' = dB_2/dT$.

The general conclusion, which is borne out for the other substances examined, is that the linear relation holds in the liquid region for $\rho \gtrsim \rho_B$. As far as we can tell, the upper density limit for the linearity in the liquid region is the freezing line.

To investigate the supercritical region, we turn first to N₂, using the summary of Jacobsen et al.⁷ A typical supercritical

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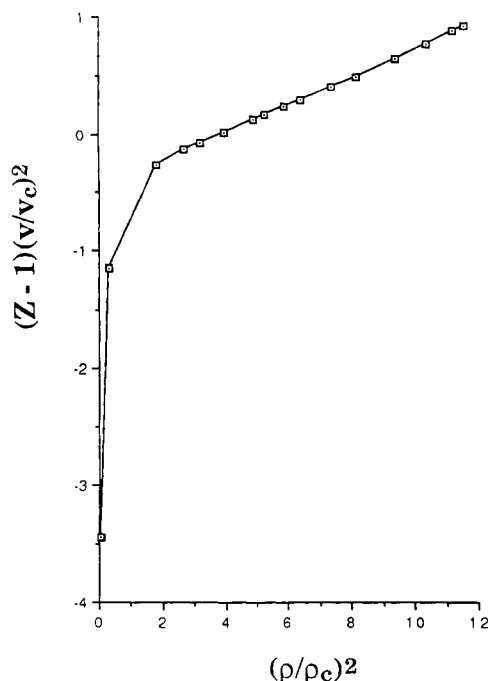
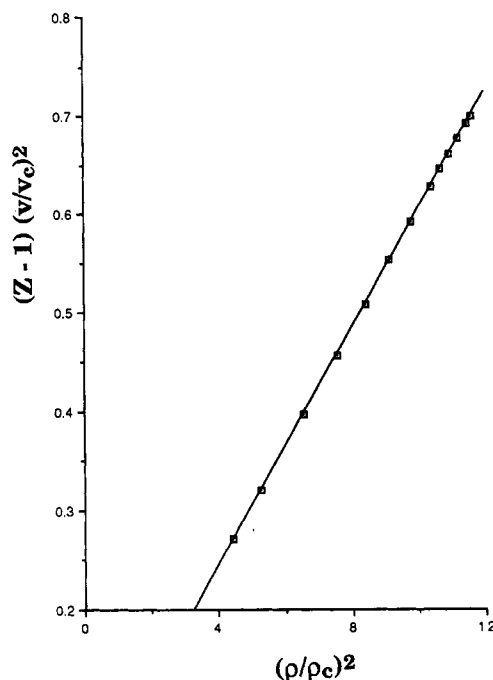
Figure 2. Same as Figure 1, for supercritical N₂ at 150 K.

Figure 3. Search for an upper density limit of the linear relation: supercritical Ar at 35 °C.

isotherm (150 K) is shown in Figure 2, in which densities are for convenience reduced by $\rho_c = 11.177 \text{ mol/L}$.⁷ Again, the linear relation holds for $\rho \gtrsim \rho_B$, where the Boyle density for N₂ is about 20 mol/L. Very marked deviations from linearity appear at lower densities. (Low-density data did not appear in Figure 1 because of condensation.)

Thus, the general rule in both the liquid and supercritical regions is that the linear relation holds for $\rho \gtrsim \rho_B$.

In order to see whether there is any upper density limit for the linearity, we use the actual high-density experimental p - v - T data for supercritical Ar,⁸ rather than a summary that involves smoothing and some extrapolation. The 35 °C isotherm is shown in Figure 3 and is linear up to the highest measured density, corresponding to $\rho/\rho_B \approx 1.85$. A similar result holds for N₂ at 35 °C, for which the measurements⁹ are linear up to the highest

TABLE I: Reduced Intercept (A) and Slope (B) of $(Z - 1)(v/v_c)^2 = A + B(\rho/\rho_c)^2$, the Coefficient of Determination (R^2), the Pressure Range (Δp) of the Data, and the Average Absolute Percent Deviation of the Calculated Density at a Given Pressure for Nitrogen^a

T, K	A	B	R^2	$\Delta p, \text{MPa}$	$100(\Delta\rho /\rho)_{av}^b$
100	-1.035 50	0.171 07	0.999	0.80-200	0.36 (0.70)
110	-0.855 75	0.154 59	0.999	1.50-250	0.52 (1.45)
120	-0.720 55	0.142 35	0.999	4.00-300	0.61 (2.16)
130	-0.624 70	0.134 36	0.999	10-400	0.50 (1.86)
140	-0.529 98	0.125 33	0.999	15-500	0.43 (1.36)
150	-0.452 94	0.117 76	0.999	20-550	0.37 (1.40)
180	-0.260 43	0.097 651	0.999	40-800	0.24 (0.69)
200	-0.164 70	0.087 130	1.000	50-1000	0.19 (0.50)
220	-0.086 327	0.077 932	1.000	60-1000	0.11 (0.38)
250	0.006 835 7	0.066 789	1.000	80-1000	0.05 (0.15)
400	0.227 67	0.037 205	1.000	150-1000	0.05 (0.18)
500	0.287 37	0.027 127	0.999	200-1000	0.09 (0.26)
600	0.322 89	0.019 957	0.997	250-1000	0.11 (0.27)
800	0.359 18	0.012 56	0.979	350-1000	0.13 (0.25)

^a Data from ref 7. ^b Maximum deviations are given in parentheses.

TABLE II: Same as Table I, for Different Fluids

fluid	T, K	A	B	R^2	$\Delta p, \text{MPa}$	$100(\Delta\rho /\rho)_{av}$
Ar ^a	100	-1.306 6	0.186 47	1.000	0.40-60	0.05 (0.08)
Ar ^a	180	-0.409 23	0.104 81	1.000	30-500	0.14 (0.27)
O ₂ ^b	120	-1.019 9	0.165 14	1.000	1.20-120	0.10 (0.19)
CO ^c	110	-0.898 84	0.150 75	0.999	1.20-100	0.22 (0.52)
CH ₄ ^d	150	-1.032 6	0.170 57	0.999	1.20-200	0.24 (0.59)
C ₂ H ₆ ^d	200	-1.550 4	0.216 80	1.000	0.30-70	0.05 (0.10)
C ₃ H ₈ ^d	300	-1.058 1	0.173 52	0.998	1.00-100	0.24 (0.55)
C ₂ H ₄ ^b	220	-0.997 66	0.157 34	1.000	1.00-20	0.02 (0.04)
C ₂ H ₂ ^e	226	-1.038 7	0.168 19	0.999	1.50-260	0.23 (1.03)
C ₆ H ₆ ^f	450	-1.139 6	0.182 43	0.999	1.00-100	0.18 (0.34)
CH ₃ OH ^g	410	-0.672 36	0.083 659	1.000	1.20-70	0.04 (0.07)
NH ₃ ^h	325	-0.701 91	0.093 685	0.999	2.20-500	0.20 (0.35)
H ₂ ^b	30	-0.650 04	0.124 00	0.999	1.00-50	1.62 (16.61)

^a Reference 6. ^b Reference 11. ^c Reference 12. ^d Reference 13. ^e Reference 14. ^f Reference 15. ^g Reference 16. ^h Reference 17.

density of $\rho/\rho_B \approx 1.95$. Therefore, as far as reported experimental data are concerned, there appears to be no known upper density limit for the linearity.

In order to find the temperature range over which the linearity holds when $\rho \gtrsim \rho_B$, we have plotted $(Z - 1)v^2$ against ρ^2 for N₂ at different temperatures. The results are summarized in Table I, including the intercept and slope of the fitted straight line, the pressure range of the data, and the average absolute percent deviation of the calculated and predicted densities for a given pressure. Because both $(Z - 1)v^2$ and ρ^2 are subject to experimental error, we also show the coefficient of determination¹⁰ R^2 , which is simply the square of the correlation coefficient. Here R^2 should be within 0.005 of unity for a straight line to be considered a good fit. From these values it appears that the linearity is good except at the highest temperature, corresponding roughly to $T \approx 2T_B$ ($T_B = 324 \text{ K}$ for N₂³). The lower temperature limit is of course the triple-point temperature, the lowest temperature at which a stable liquid phase exists.

To see whether the regularity is limited to a certain type of fluid or is generally true, we have plotted $(Z - 1)v^2$ against ρ^2 for a number of different fluids at different temperatures. The linearity seems to hold as long as $\rho \gtrsim \rho_B$. The various fluids tested are listed in Table II, together with the intercept, slope, pressure range of the experimental data,^{6,11-17} and the coefficient of determination and average absolute percent deviation of the calculated density for a typical isotherm. Most of these isotherms correspond approximately to $T \approx 0.8T_c$, that is to liquids, but for Ar we show the results for one subcritical and one supercritical isotherm ($T_c = 150.66 \text{ K}$ for Ar³). Notice that the list includes the polar fluids CH₃OH and NH₃ and the quantum liquid H₂. We conclude that the linearity is a property of many types of

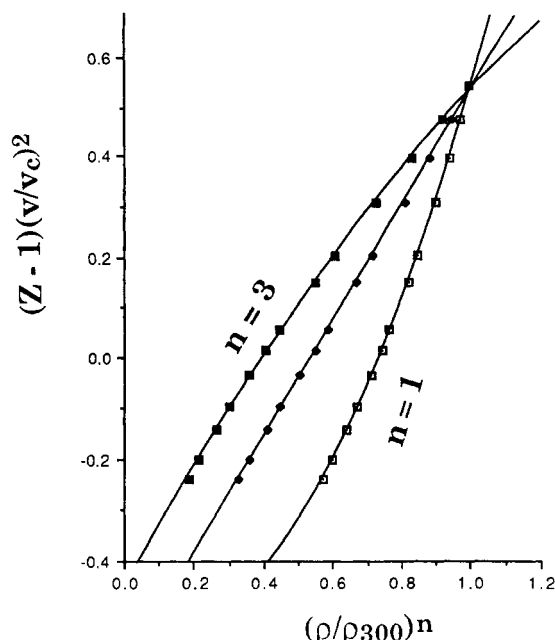


Figure 4. Test of the linearity of $(Z-1)v^2$ vs ρ^n for $n = 1, 2, 3$, for Ar at 150 K. The density scale is reduced by ρ_{300} , the density at 300 MPa.

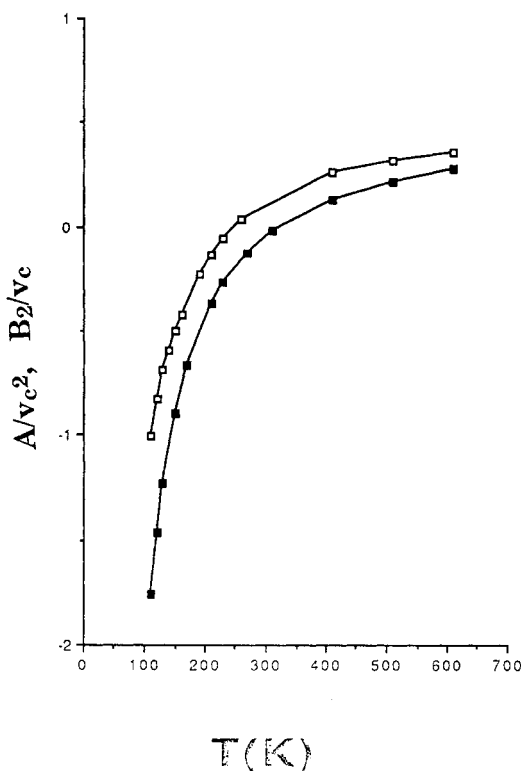


Figure 5. Comparison of the temperature dependences of the intercept parameter A (\square) and the second virial coefficient B_2 (\blacksquare) for N_2 , both made dimensionless with v_c .

dense fluids, although we have not yet examined metals or strongly hydrogen-bonded fluids.

Finally, we test how sensitive the linearity of $(Z-1)v^2$ is with respect to the power of ρ . The reason for this concern is that in the original lattice-type model⁵ the power of ρ depended explicitly on the 12th power repulsion of the Lennard-Jones potential. In Figure 4 we show a typical plot of $(Z-1)v^2$ vs ρ^n for $n = 1, 2$, and 3, for the 150 K isotherm of supercritical Ar. It is apparent that the isotherm turns upward for $n = 1$ and downward for $n = 3$ and is nearly linear only for $n = 2$.

A feature of the regularity that seems to invite some theoretical investigation is the temperature dependence of the intercept and

slope of $(Z-1)v^2$ vs ρ^2 . For instance, examination of the numerical values of the intercept given in Table I for N_2 shows a remarkable similarity to the temperature dependence of the second virial coefficient. The similarity is shown in Figure 5, using tabulated values¹⁸ of the second virial coefficient.

Temperature Dependence of Parameters

We present here a simple model that mimics the linearity of $(Z-1)v^2$ vs ρ^2 and predicts the temperature dependence of its parameters. We begin with the exact thermodynamic relation

$$p = T(\partial p / \partial T)_\rho - (\partial E / \partial V)_T \quad (1)$$

in which $T(\partial p / \partial T)_\rho$ is usually called the thermal pressure and $(\partial E / \partial V)_T$ is called the internal pressure.¹⁹ For example, for a van der Waals fluid the thermal pressure is $RT/(v-b)$ and the internal pressure is a/v^2 . We can divide the thermal pressure into two contributions: an ideal contribution, RT/v , and a nonideal contribution, which is $RTb/v(v-b)$ for a van der Waals fluid.

We attempt to calculate the internal pressure by modeling the average configurational potential energy and then taking its derivative with respect to volume. We assume that any kinetic energy contribution to the internal energy E will vanish on taking the derivative, since the temperature is held constant. We approximate the average potential energy by summing the contribution from nearest neighbors only, assuming single inverse powers for the effective repulsion and attraction, and obtain

$$U = \frac{N}{2} z(\rho) \left(\frac{C_n}{\bar{r}^n} - \frac{C_m}{\bar{r}^m} \right) \quad (2)$$

where U is the total potential energy among N molecules, $z(\rho)$ is the average number of nearest neighbors, \bar{r} is the average distance between nearest neighbors, and C_n and C_m are constants. We taken $z(\rho)$ to be proportional to ρ , as is the case for liquid argon, rubidium, and cesium,²⁰ and taken $v \sim \bar{r}^3$, so that U can be written as

$$\frac{U}{N} = \frac{K_n}{v^{n/3+1}} - \frac{K_m}{v^{m/3+1}} \quad (3)$$

where K_n and K_m are constants. Carrying out the differentiation, we find the internal pressure to be

$$p_{\text{int}} = \left(\frac{\partial E}{\partial V} \right)_T \approx \left[\frac{\partial (U/N)}{\partial v} \right]_T = A_1 \rho^{m/3+2} - B_1 \rho^{n/3+2} \quad (4)$$

where A_1 and B_1 are constants.

Combining the foregoing results, we have

$$(Z-1)v^2 = \frac{-A_1}{RT} \rho^{m/3-1} + \frac{B_1}{RT} \rho^{n/3-1} + \frac{1}{\rho^2} \left[\frac{1}{\rho R} \left(\frac{\partial p}{\partial T} \right)_\rho - 1 \right] \quad (5)$$

in which the last term arises from the nonideal contribution to the thermal pressure. In order to model the experimental results, we should take $m = 3$ and $n = 9$ and have the last term of eq 5 be nearly constant in the density range of interest. This last expectation is somewhat surprising but is borne out for real fluids. For example, for Ar in the density range of interest, the last term of eq 5 varies by about 8% while the term $(Z-1)v^2$ varies by 100%. Some reason for this behavior can be obtained in a simple way by considering a van der Waals fluid. The expression within the brackets is equal to $b\rho(1-b\rho)$, and this is multiplied by $1/\rho^2$. The whole term is independent of temperature and diverges at both $\rho = 0$ and $b\rho = 1$, but at intermediate densities it varies rather slowly, with a minimum at $b\rho = 1/2$. It is thus at least plausible that the last term of eq 5 should be nearly constant in the range of interest, with only a weak dependence on temperature and density. This is in fact verified by experiment, and it is therefore a reasonable approximation to replace the term by a constant, A_2 .

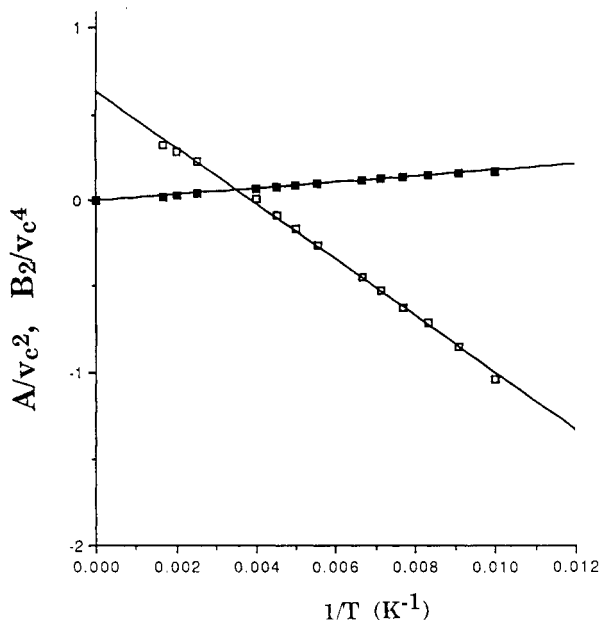


Figure 6. Temperature dependence of the reduced intercept parameter A (\square) and the reduced slope parameter B (\blacksquare), for N_2 .

The final result is therefore of the form

$$(Z - 1)v^2 = A + B\rho^2 \quad (6)$$

where $A = A_2 - A_1/RT$ and $B = B_1/RT$. The model thus not only mimics the linearity of $(Z - 1)v^2$ vs ρ^2 but also predicts the temperature dependence of the intercept and slope. This result immediately shows why A has such similarity to the second virial coefficient—it has the same temperature dependence as that of a van der Waals gas, whose second virial coefficient is $b - a/RT$, which usually gives a fair representation of the temperature dependence for real gases in the vicinity of T_B .

The intercept A is predicted to be linear in $1/T$, and the slope B to be proportional to $1/T$, and this turns out to be quite a good approximation, as shown by the example of N_2 plotted in Figure 6. Some deviations appear at the highest temperatures ($T > T_B$), a not unexpected result inasmuch as the model ascribes all of the internal pressure to potential energy, which is an approximation that should be best at lower temperatures.

Comparison with Equations of State

Equations of state (EOS) based on statistical-mechanical perturbation theory are available, and these can be checked for consistency with the linearity of $(Z - 1)v^2$ vs ρ^2 . However, it is worthwhile to look first at the simpler van der Waals EOS, even though it is quantitatively inaccurate, since its success or failure can indicate what features of an EOS are crucial for the explanation of a phenomenon. Moreover, in some sense it can be regarded as an exact theoretical result for a definite, although physically unrealistic, model of hard spheres with weak long-range attractive forces.²¹

For the van der Waals EOS, $v_B = b$ and $T_B = a/bR$, and the EOS can be arranged into the dimensionless form

$$(Z - 1)(v/v_B)^2 = \frac{1}{b\rho} \left(\frac{1}{1 - b\rho} - \frac{T_B}{T} \right) \quad (7)$$

It is obvious that the right-hand side of eq 7 does not vary in general as ρ^2 , but if it is plotted against $(\rho/\rho_c)^2$, there is an appreciable linear portion. This is shown in Figure 7 for several isotherms. To make comparisons with Figures 1–3 easier, the volumes and densities have been reduced by the critical volume, $v_c = 3b$. For $b\rho \rightarrow 1$, the term $(1 - b\rho)^{-1}$ causes the expression to diverge. This divergence can be attributed to the intermolecular repulsion. For $b\rho \rightarrow 0$ and $T < T_B$, the term $(T_B/T)(b\rho)^{-1}$ causes

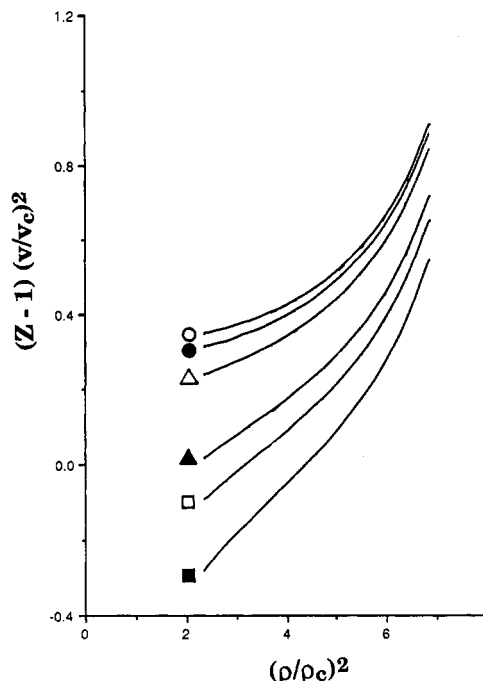


Figure 7. van der Waals isotherms of $(Z - 1)v^2$ vs ρ^2 , showing the region of linearity, for $T/T_B = 0.3$ (\blacksquare), 0.4 (\square), 0.5 (\blacktriangle), 1.0 (\triangle), 1.5 (\bullet), and 2.0 (\circ).

the expression to approach negative infinity. Since T_B is proportional to the van der Waals a , this divergence can be attributed to the intermolecular attraction. However, the balance between attraction and repulsion leads to an inflection point and hence to a nearly linear portion in the density range $2.5 < (\rho/\rho_c)^2 < 5$. For $T > T_B$ the attraction loses out and the curves diverge to positive infinity at zero density, but a linear portion still persists up to about $T \approx 2T_B$.

From the van der Waals EOS we can thus draw three tentative conclusions. First, the linear regime does not depend on any special features of molecular interactions but only on the existence of long-range attraction and short-range repulsion. In contrast, the existence of the common bulk modulus point requires a particular temperature dependence for the covolume b .²² Second, the linear region results from a balance between the attraction and the repulsion. Third, there are bounds on the range over which the linearity is expected to hold: an upper bound for T and both a lower and upper bound for ρ , although this latter bound does not show up in the existing experimental data.

The foregoing conclusions can be tested and made more precise by means of an accurate EOS based on statistical-mechanical perturbation theory, modified by a new strong principle of corresponding states.²³ This EOS can be written in a form analogous to eq 7 as

$$(Z - 1)v^2 = \frac{1}{\rho} \left(\frac{\alpha}{1 - \lambda b\rho} - \frac{\alpha - B_2}{1 + \delta b\rho} \right) \quad (8)$$

where B_2 is the second virial coefficient, α is a temperature-dependent parameter that scales for the softness of the repulsive forces and is equal to the contribution of the repulsive forces to B_2 , and b is a temperature-dependent analogue of the van der Waals covolume related to α by $b = d(\alpha T)/dT$. The constants δ and λ are characteristic of the particular fluid, but δ is only a small correction for some secondary effects of the attractive forces and can be taken equal to 0.22λ for practical purposes. The constant λ is equal to 0.454 for the noble gases and is smaller for other substances. If $B_2(T)$ is known, then $\alpha(T)$ and $b(T)$ can be calculated from simple scaling rules.²³ Several reduced isotherms of $(Z - 1)(v/v_B)^2$ as a function of $(\rho/\rho_B)^2$ are shown in Figure 8 for $\lambda = 0.454$. The results are very similar to those for the van

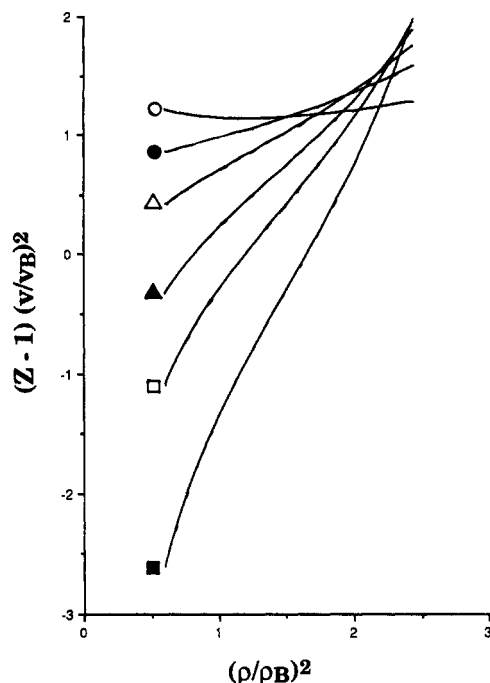


Figure 8. Isotherms of $(Z - 1)v^2$ vs ρ^2 for the Ihm-Song-Mason EOS, eq 8, showing the region of linearity, for $T/T_B = 0.3$ (■), 0.4 (□), 0.5 (▲), 0.7 (△), 1.0 (●), and 2.0 (○).

der Waals isotherms of Figure 7, the main difference being only in the scale of densities over which the isotherms are nearly linear, which is $1 \leq (\rho/\rho_B)^2 \leq 2$. Thus, the previous conclusions from the van der Waals EOS are essentially confirmed, especially the fact that the linear region results from a balance between the attractive and repulsive forces. The predicted upper temperature bound for the linear region ($T < 2T_B$) is also confirmed and is in accord with the experimental data, as is the predicted lower density bound of $\rho \gtrsim \rho_B$. The upper density bound is predicted to be about $\rho \lesssim 1.4\rho_B$, however, which is less than the observed value of at least $1.85\rho_B$ for Ar (Figure 3) and at least $1.95\rho_B$ for N_2 .

Discussion

The linearity of $(Z - 1)v^2$ vs ρ^2 has been checked with experimental measurements. A simple model that mimics the linearity has been used to predict the temperature dependences of the intercept and slope parameters and shown to agree with experiment. The existence of the linear region has been shown to be consistent with the van der Waals EOS and with a more accurate statistical-mechanical EOS, although the measurements have a larger range of linearity than suggested by the EOS. The calculations all suggest that the linear region is due to a balance between intermolecular attractive and repulsive forces. To further test this suggestion, we compare the mean molecular separation, \bar{r} , over the experimental linear density range with the position of the minimum of the pair potential, r_m , for a number of fluids^{23,24} in Table III. The true range of \bar{r} is probably greater than shown in Table III, because the measurements seldom cover the entire linear range. As can be seen, the value of r_m is more or less within the range of \bar{r} .

The range of density and temperature over which the linear relation is valid can be approximately specified as follows. The lower density limit is approximately the Boyle density ρ_B , for all temperatures from the triple point up to about $2T_B$, which is far into the supercritical region, roughly $5T_c$. The upper density limit is less certain. In the true liquid state ($T < T_c$), the limit seems to be the freezing line. In the supercritical region ($T > T_c$), the statistical-mechanical EOS indicates that the limit of validity is about $1.4\rho_B$ (about $2.5\rho_c$), whereas the experimental

TABLE III: Mean Molecular Separation in the Linear Density Range Compared to the Equilibrium Pair Potential

fluid	T, K	$\rho, \text{mol/L}$	$\bar{r}, \text{\AA}$	$r_m, \text{\AA}$
Ar	150	23.041–40.397	3.45–4.16	3.82 ^b
N_2	200	20.562–40.977	3.44–4.32	4.13 ^c
O_2	120	30.47–38.12	3.52–3.79	3.88 ^b
CO	110	23.157–30.727	3.78–4.16	4.22 ^b
CH_4	150	22.36–30.21	3.80–4.20	4.18 ^c
C_2H_6	200	17.44–19.24	4.42–4.57	4.44 ^b
C_3H_8	300	11.1–13.7	4.95–5.31	5.43 ^c
C_2H_2	226	16.985–23.261	4.15–4.61	4.74 ^b
CH_3OH	410	20.758–23.513	4.13–4.31	4.11 ^b
NH_3	325	32.869–45.111	3.33–3.70	
H_2	30	27.42–45.49	3.32–3.93	3.22 ^b

^a Data from sources cited in Table II. ^b Reference 24. ^c Reference 23.

data do not set an upper limit, other than that it is at least $1.95\rho_B$ (about $3.5\rho_c$) for N_2 . Thus, the method of plotting $(Z - 1)v^2$ vs ρ^2 reveals a small inaccuracy of the EOS in the dense supercritical fluid region.

It has been emphasized by Xu and Herschbach³ that the Zeno line provides a significant constraint on equation-of-state relationships. The present linear relation provides some points on the Zeno contour, and these do indeed fall on a straight line, but the points fall only on the low-temperature, high-density section of the Zeno line. In particular $\rho_B \approx 0.5\rho_Z$, where ρ_Z is the (extrapolated) density on the Zeno line at $T = 0$, and this corresponds to a temperature of $0.5T_B$. Thus, the present relation overlaps the Zeno line only for temperatures above freezing and below about $0.5T_B$ (about $1.3T_c$). As a result, if the Zeno line is known, it furnishes a useful check on the present results, but the range of the present results is too small to give reliable information on a completely unknown Zeno line.

The present results have several obvious applications. At the simplest level, we now have a new and useful way of plotting data on the isotherms of compressed dense fluids. Moreover, the temperature dependences of the two constants that characterize each linear isotherm are known: the intercept A is linear in $1/T$ and the slope B is proportional to $1/T$ (Figure 6). Thus, only two isotherms need to be measured in order to predict all the others. It is therefore possible, for instance, to predict the behavior in the supercritical region from measurements made in the subcritical region.

Finally, we expect the linearity of $(Z - 1)v^2$ vs ρ^2 to hold for dense mixtures as well as for single substances. The reason for this expectation is the well-known success of so-called one-fluid approximations for mixtures. Such approximations assume that mixtures obey the same EOS as single substances, but with parameters that depend on the composition of the mixture.²⁵ Since the present linearity has been shown to be consistent with an EOS, adjusting the parameters of the EOS for compositions will not alter this result. Testing of this expectation and investigation of the composition dependences of the parameters A and B remain for future work.

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