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Volumetric Properties of Fluids Calculated by Renormalization-Group Theory[1]

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A renormalization-group theory has been developed recently with which to calculate thermal properties of fluids throughout an extended neighborhood of their gas–liquid critical point. In tests performed to date, the theory has proved capable of predicting volumetric properties to ~1% accuracy (for pressures near the critical point and densities elsewhere) for several different fluids when applied in a very simple approximation that requires adjustment of at most three constants. Results are presented for these initial investigations. Comparison is made both with experimental data and with predictions of simple microscopic models of the underlying intermolecular forces.

KEY WORDS: global renormalization group; supercritical fluid; volumetric properties.

1. INTRODUCTION

An effort has been made recently [1–3] to develop a global renormalization-group theory of fluids together with an approximation scheme for carrying through practical calculations to make it possible to predict thermal behavior of fluids to improved accuracy when information from experiments is lacking or very limited. One goal is to be able ultimately to make predictions accurately from a knowledge of underlying intermolecular interactions. Some progress in that direction will be reported here. Another objective is to make predictions over large ranges of density and temperature when data from experiments is limited to small portions of those ranges. Progress in this area will be illustrated below by some examples of the accuracy currently attainable from a knowledge of just one, two, or three appropriately chosen (P, V, T) data points.

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A renormalization-group approach was chosen in formulating the theory so that contributions to the free energy that come from spontaneous fluctuations of density within the fluid should be correctly taken into account. A proper accounting of the density fluctuations is essential for any accurate, fundamental theory of behavior near the critical point: it is well known to be needed there to understand the nonanalytic behavior of thermodynamic functions, the nonclassical values of critical point exponents, etc. But even at quite large distances from the critical point, for example, at critical temperature, but 50% greater than critical density, the non-mean-field behavior of the fluctuations has been found to account for a large portion of some measured quantities, e.g., the pressure [4].

There is thus, from a fundamental point of view, a need to consider fluctuations properly, including when considering nonuniversal properties such as the pressure, temperature, and density measured at the critical point and also when not especially close to the critical point. Until quite recently, however, it appears not to have been possible to use existing renormalization-group ideas directly to treat properties of fluids, or of the many other systems that have second-order phase transitions (critical points), except for some universal behaviors that are observed in a quite small neighborhood about the critical point. The theory used in the present investigation is a generalization of earlier renormalization treatments to include nonuniversal aspects of the fluctuations and to take into account their contributions even when not close to the critical point. A mathematical discussion of the extensions of earlier renormalization treatments has been given elsewhere [3]. In particular, Section III.B in Ref. 3 is of especial importance for the work reported here.

2. RESULTS. COMPARISONS WITH EXPERIMENTS

The investigations reported here used the renormalization theory of fluids evaluated in the phase-space cell approximation as described in Ref. 3. As discussed more fully there, the renormalization-group calculations were applied to the attractive part of the intermolecular potential, assumed to be pure two-body attraction. The repulsive part of the potential was treated in the Carnahan–Starling hard-sphere approximation, with temperature- (but not density-) dependent sphere volume. In some of the work to be discussed, one hard-sphere high virial coefficient (in different gases, the 8th or the 12th) was artificially enhanced to give improved agreement with pressures measured at densities more than approximately 70% above critical.

Figure 1 illustrates results obtained for ^{3}He. The symbols are experimental data obtained by Wallace and Meyer [5]. The solid lines were calculated by adjusting just two constants in the theory. The first constant, the "cohesion volume" c [see Eq. (15a) in Ref. 3], was adjusted to make the calculated critical point match that determined experimentally. The second constant, V_1, the temperature coefficient of the hard-sphere "core" volume [see Eq. (18) in Ref. 3], was adjusted to bring theory into agreement with one pressure-density data point at a temperature different from critical. (For ^{3}He, no adjustment was made in any of the hard-sphere high virial coefficients.) Overall agreement is seen to be rather good over the range of densities and temperatures shown. Existing data do not extend to high enough temperatures to establish whether the temperature exponent for the core volume should be −0.25, as used in Ref. 3 and employed for Fig. 1, or a larger (absolute) value, more characteristic of quantum behavior. (The de Broglie wavelength for ^{3}He at its critical point is 5.5 Å, which is comparable to the average separation between ^{3}He atoms at the critical point density of 1 atom per 121 Å^3.) It is to be noted that the hard-sphere temperature coefficient required for ^{3}He was exceptionally large (see Table I). If this temperature dependence was ignored, and the spheres treated as constant in diameter ($V_1 = 0$), then agreement with experiment worsened quite conspicuously at the temperatures farthest from critical, but not noticeably for the isotherm closest to critical. (Precisely *at* the critical point temperature, of course, V_1 had *no* effect at all; the entire critical temperature isotherm was determined after a choice had been made for the single fitting constant, c = cohension volume.)

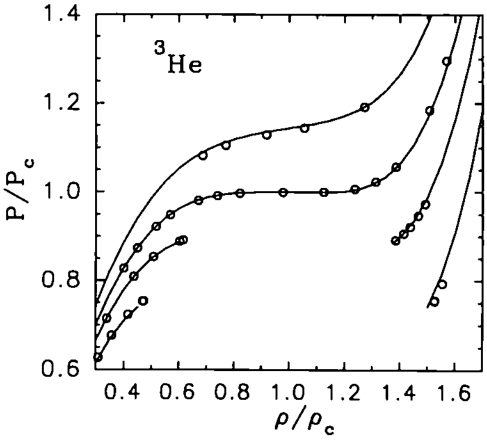

Fig. 1. Pressure isotherms for ^{3}He. Experimental data are from Ref. 5. Temperatures (from top to bottom) T_r = 1.0402, 0.9999, 0.9666, 0.9197.

Table I. Survey of Several Gases: Compressibility Ratio Z_c, Acentric Factor ω, Model Parameters c, Γ'_1, and Γ'_{12}, and rms Error

Gas	Z_c	ω	$c/4.66b_c$	Γ'_1	Γ'_{12}	rms (%)
^{3}He	0.303	−0.473	1.00	2.26	[a]	0.42
H_2	0.302	−0.216	0.97	0.70	[a]	0.39
Ar	0.291	0.001	0.80	0.06	0.023	0.65
CH_4	0.288	0.011	0.74	0.09	0.017	0.78
C_2H_6	0.285	0.099	0.67	−0.20	0.017	1.04
n-Pentane	0.263	0.251	0.54	−0.56	0.020	1.13

[a] See text.

For hydrogen (H_2), a more extensive set of volumetric data was available [6]. Adjusting just the single constant c = cohesion volume in the theory resulted in good agreement for temperatures within a few percent of critical and densities out to about 170% of critical. Adjusting the second constant, Γ'_1, thereby giving a temperature dependence to the repulsive core of the molecules, improved the agreement farther from the critical temperature, but did not eliminate the disagreement for densities greater than about 170% of critical. Therefore, for H_2, a third fitting constant was introduced, as had been done for *n*-pentane [3]. For H_2, slightly better agreement was obtained by enhancing the 8th virial coefficient, Γ'_8, rather than the 12th, Γ'_{12}, as was done for pentane [see Eq. (17) in Ref. 3]. The numerical value $\Gamma'_8 = 0.094$ was determined by the requirement that there be good agreement with one PVT data point for H_2 that had been measured at near critical temperature and a density somewhat greater than twice that at the critical point.

The overall agreement with measured volumetric properties of H_2 obtained in this way, by adjusting the three constants c, Γ'_1, and Γ'_8, is seen in Fig. 2 to be similar to that for ^{3}He (Fig. 1), but now extends considerably farther in temperature and density, well outside the range of experimental data that were available for ^{3}He. The numerical value used for Γ'_1 differed greatly from that for ^{3}He (see Table I). The de Broglie wavelength (2.1 Å) for H_2 at its critical point temperature is considerably smaller than that for ^{3}He, which has a much lower critical temperature. Also, it may be noted that, though the compressibility ratio $Z_c = P_c V_c / RT_c$ at the critical point is nearly the same for ^{3}He and H_2, the Pitzer "acentric" factors are rather different (Table I). [The acentric factor is defined as $\omega = \log_{10}(P_c/P_v) - 1$, where P_v is the vapor pressure at $T = 0.7T_c$.] Other comparisons listed in Table I include the ratio of cohesion volume c to repulsive core volume at the critical point temperature, b_c, normalized (via the factor 4.66) to unity for ^{3}He for purposes of the comparisons, and entries in the table under the heading rms. The latter entries are the root-mean-square percentage deviations between the measured data points and theory. Approximately, these deviations express the smaller of density error or pressure error at each data point; more precisely, each deviation is the distance of closest approach of the theory to the measured data point, computed from percentage errors evaluated separately for pressure and density predictions at the given temperature.

Table I summarizes results obtained for several other gases by adjusting the three constants c, V'_1, and V'_{12}. The gases include argon, methane, ethane, shown in Fig. 3, and *n*-pentane, considered previously (see Fig. 3 in Ref. 3). For argon, results obtained here are a little, though not greatly, better than were obtained in an earlier investigation of argon using a soft-sphere model and adjusting, rather than V'_1 and V'_{12}, instead two constants associated with modifications of the third and fourth virials in that model. [See Ref. 2, especially Figs. 1c and 1d, and the statement made in Ref. 2 in the next to bottom line on p. 62.] Results obtained for argon using the present model in the simpler approximation of hard spheres with temperature-independent core volumes and no high virial correction ($V'_1 = V'_{12} = 0$) so only the single constant c = cohesion volume is adjusted (to make the theory give the correct pressure at the critical point) are very nearly the

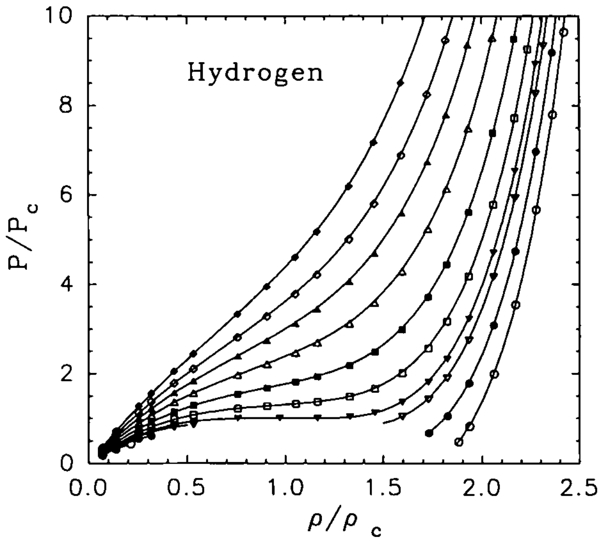

Fig. 2. Pressure isotherms for H_2. Temperatures T_r = 1.668, 1.516, 1.395, 1.274, 1.152, 1.061, 1.001, 0.970, 0.910, 0.849. Experimental data from Ref. 6.

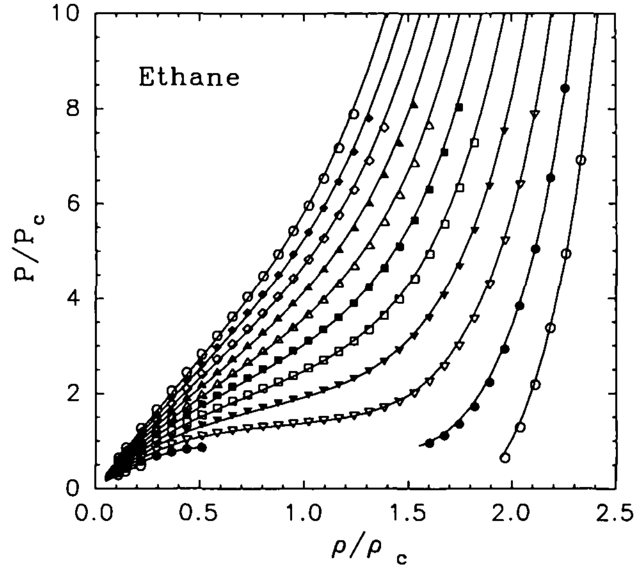

Fig. 3. Pressure isotherms for ethane. Temperatures $T_r = 1.713$, 1.632, 1.550, 1.468, 1.386, 1.304, 1.222, 1.140, 1.058, 0.976, 0.895. Experimental data from Ref. 7.

same as shown previously in Ref. 4 and in Figs. 1–6 of Ref. 1 for generic "simple" fluids treated in that approximation. In that approximation, the agreement for argon and the other simple fluids is found to be good for a somewhat wider range of temperatures than for H_2 but for a similar range of densities—i.e., out to about 170% of critical.

3. MICROSCOPIC MODELING

An important goal of the present research is to be able to predict thermal behavior of fluids, including near the critical point, from a characterization of the underlying microscopic intermolecular interactions. As steps in that direction, it is of interest to see how well (or badly) some simple microscopic models predict the observed critical point properties and to investigate how the parameter values in a particular model needed to give correct critical point properties when used in the present theory vary among the different fluids studied.

Consider first argon. The two-parameter, Lennard-Jones model does not work especially well for argon. But various three-parameter models are capable of predicting exactly the critical point temperature, density, and

Table II. Square-Well Parameters That Give Correct Critical Point P, V, T When Employed in the Theory Used Here

Gas	σ (Å)	ε/k (K)	R
^{3}He	3.19	1.53	1.92
H_2	3.03	15.9	1.90
Ar	3.23	97.1	1.75
CH_4	3.55	138	1.70
C_2H_6	4.05	264	1.63
n-Pentane	5.21	598	1.49

pressure when employed in the present theory. One example is a model potential that is Lennard-Jones from $r = \infty$ to the minimum, $-\varepsilon$, at $r = 2^{1/6}\sigma$, then constant, equal to $-\varepsilon$, until $r = \sigma_i < \sigma$, and thereafter infinite for all smaller r. The argon critical point is predicted correctly by the present theory using this model if $\sigma = 3.508$ Å, $\varepsilon/k_B = 117.6$ K, and $\sigma_i = 3.227$ Å. The values for σ and ε/k differ not greatly from Lennard-Jones values obtained by fitting to the temperature dependence of the second virial coefficient suggested in Ref. 8 ($\sigma = 3.405$, $\varepsilon/k = 119.8$) or more recently [9] ($\sigma = 3.504$, $\varepsilon/k = 117.7$) or ($\sigma = 3.400$, $\varepsilon/k = 116.80$) obtained in a somewhat different way [10]. Using a square-well model (infinite potential for $r < \sigma$, $-\varepsilon$ for $\sigma < r < R\sigma$, and zero for all larger r), the argon critical point is predicted correctly by using in the present theory $\sigma = 3.227$ Å, $\varepsilon/k = 97.1$ K, $R = 1.75$. Investigations of the second virial coefficient of argon have resulted in proposed square-well model parameters (σ, ε/k, R) equal to [8] (3.162 Å, 69.4 K, 1.85) and [9] (3.067 Å, 93.3 K, 1.70). There is serious disagreement between the present values and those noted in Ref. 8, but agreement to within $\simeq 5\%$ with the parameter values proposed in Ref. 9. In Table II the square-well parameter values found in the same way as for argon are listed for all of the gases considered here.

4. DISCUSSION

The recently developed global renormalization-group theory for fluids [3] has been applied in simple approximation to several different gases whose compressibility ratio $Z = PV/RT$ at the critical point ranges from slightly higher than 0.30 (^{3}He and H_2) to 0.26 (n-pentane) and whose Pitzer acentric factor ranges from -0.47 to $+0.25$. For these gases the agreement between predicted and measured pressures near the critical point and densities elsewhere averages approximately 1% for a reasonably wide range of densities and temperatures [roughly $(0.2\text{–}2.4)\rho_c$ and

$(0.85-1.7)T_c$, for pressure to $\sim 10P_c$]. The theory is capable of predicting critical point pressure, temperature, and density from a characterization of the underlying intermolecular interactions. To illustrate, square-well model parameters were quoted which, when used in the present theory, yield the experimentally observed critical point properties for each of the gases considered.

REFERENCES

1. L. W. Salvino and J. A. White, *J. Chem. Phys.* **96**:4559 (1992).
2. J. A. White, *Fluid Phase Equilibria* **75**:53 (1992).
3. J. A. White and S. Zhang, *J. Chem. Phys.* **99**:2012 (1993).
4. J. A. White, in *The Physics of Phase Space*, Y. S. Kim and W. W. Zachary, eds. (Springer, Berlin, 1987), p. 72.
5. H. Meyer, private communication.
6. R. D. Goodwin, D. D. Diller, H. M. Roder, and L. A. Weber, *J. Res. NBS* **67A**:173 (1963).
7. D. R. Douslin and R. H. Harrison, *J. Chem. Thermodynam.* **5**:491 (1973).
8. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
9. A. E. Sherwood and J. M. Prausnitz, *J. Chem. Phys.* **41**:429 (1964).
10. T. Boublik, *J. Chem. Phys.* **87**:1751 (1987).