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Perturbation Theory and Equation of State for Fluids

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In the perturbation theory studied by Barker and Henderson, an expansion is made of the free energy in terms of a strength parameter λ that multiplies the attractive part of the potential. This expansion is shown here to converge very rapidly for the Lennard-Jones liquid. Taking as zeroth-order approximation the system with only repulsive forces, Barker and Henderson have shown that it can be approximated by hard spheres with a temperature-dependent diameter. We show by a direct computation that this approximation is excellent. In the spirit of the λ expansion, we can write down a semiempirical equation of state which is applied with success to the Lennard-Jones fluid, argon, and xenon. It is seen that the large scale density variation characteristic of the critical point lowers the critical temperature by 6%.

I. INTRODUCTION

Two recent papers by Barker and Henderson[1] again call attention to the perturbation theory proposed by Zwanzig[2] for the study of classical fluids: The attractive part of the intermolecular potential is multiplied by a strength parameter λ, and the free energy is expanded as a power series in λ, around $\lambda = 0$. This λ expansion, further studied by various authors,[3] is to be contrasted with the γ expansion of Hemmer[4] and of Baer, Lebowitz, and Stell,[5] which is an expansion, in the spirit of the van der Waals theory, in terms of the inverse range γ of the attractive part of the potential. Brout and Coopersmith's approach[6] is a mixture of λ and γ expansion.

Zwanzig's theory was devised for a potential possessing a real hard core. In that case the λ expansion is simply the inverse temperature expansion. Barker and Henderson make a very ingenious generalization of Zwanzig's theory to the case of a two-body potential of the Lennard-Jones type. Furthermore a specific approximation for the second-order term of the perturbation enables Barker and Henderson to derive an equation of state which agrees well with the results of computer simulations. In view of this success we believe it is useful to examine critically the various aspects of their theory.

Let us first remind the reader of the perturbation theory referred to above. Let the interaction between the atoms be the Lennard-Jones potential,

$$\Phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \quad ,$$

which we shall divide into two parts: a short-range part $u(r)$ for $r < \sigma$, and a longer-range attractive part $w(r)$ for $r > \sigma$. It is easy to see that the Helmholtz free energy is given by

$$F/NkT = F_0/NkT + \int_0^1 d\lambda \langle W \rangle_\lambda /NkT \quad . \tag{1}$$

Here F_0 is the free energy of a system of particles interacting through $u(r)$ only, which we call the reference system. $\langle W \rangle_\lambda$ is the average of the attractive part of the interaction

$$\sum_{i<j} w(|\vec{r}_i - \vec{r}_j|) \quad ,$$

when the particles interact through a potential $u(r) + \lambda w(r)$. This potential gives rise to a radial distribution function $g(r, \lambda)$. We have explicitly

$$\langle W \rangle_\lambda /NkT = \tfrac{1}{2}\rho\beta \int d\vec{r}\, g(r,\lambda) w(r) \quad , \tag{2}$$

where ρ is the particle density and $\beta = 1/kT$.

For liquid densities, the gross features of the radial distribution function are determined by the presence of the repulsive core. It is therefore tempting to replace, in first approximation, $g(r, \lambda)$ by $g(r, 0) = g_0(r)$. This is the physical basis of the λ expansion.

In Sec. II, we present a direct computation of $\langle W \rangle_\lambda /NkT$ for a state not far from the triple point. There it is shown that the rate of convergence of the λ expansion is very good and that it is an excellent approximation to retain only the second-order term, in addition to $\langle W \rangle_0 /NkT$, as Barker and Henderson have done. That term involves the fluctuations of the attractive part of the potential, evaluated for the reference system.

The whole approach presupposes that we can give an adequate treatment of the reference system. Barker and Henderson, using a perturbation theory where the inverse steepness of the repulsive potential is the expansion parameter, succeed in replacing the interaction $u(r)$ by a hard-core potential of diameter d, where d is given by

$$d=\int_0^\sigma dz\,(1-e^{-\beta u(z)})\ . \tag{3}$$

Then using results for the hard-sphere gas obtained from machine computation, it is possible to evaluate the thermodynamics of the reference system.

It is shown in Sec. III by a direct comparison with an "exact" (Monte Carlo) treatment of the reference system that, at this stage, the Barker-Henderson approximation is outstandingly good.

The first-order term $\frac{1}{2}\beta\rho\int d\vec{r}\,g_0(r)w(r)$, must then be evaluated. $g_0(r)$ is replaced by the radial distribution function for the hard-sphere gas of diameter d in the Percus-Yevick approximation. This is shown to lead to an error of the order of 2%.

We then proceed (Sec. IV) to discuss the approximation introduced by Barker and Henderson for the evaluation of the complicated second-order term. It is shown that their approximation for it is of the right order of magnitude, but is quantitatively incorrect.[7]

In Sec. V, we use the basic ideas of the λ expansion together with the Barker-Henderson treatment of the repulsive core to derive semi-empirical equations of state that fit the data obtained from machine computation results in the liquid and dense gas region. These equations of state contain only a few parameters and fit very well the machine data, which are reviewed in the Appendix.

We give in Sec. VI examples of the application of these equations to the calculation of the fundamental thermodynamic functions and of their derivatives.

In Sec. VII, equations of state are derived for argon and xenon. From these equations it is concluded that, for moderate temperatures, the core of argon is narrower and steeper than indicated by the Lennard-Jones potential; that the diameter of the xenon core is 4% larger than that deduced from the study of the second virial coefficient; and that the suppression of the large scale density variations characteristic of the critical region would have the effect of raising the critical temperature by 6%.

II. VALIDITY OF THE λ EXPANSION

We first proceed to investigate the validity of the λ expansion by considering the specific example of a liquid in a state not far from the triple point: $\rho=0.85$, $T=0.72$. The direct Monte Carlo computation of $\langle W\rangle_\lambda/NkT$ was made for five values of λ: $\lambda=0$, 0.25, 0.5, 0.75, and 1. The results are shown in Fig. 1, where

$$(\langle W\rangle_\lambda-\langle W\rangle_0)/NkT$$

is plotted as a function of λ. We see that this plot is not far from linear. This shows that keeping terms up to the second order in λ will yield good results. Specifically we have $\langle W\rangle_0/NkT=-7.79$. For the curve of Fig. 1, we can calculate the contribution to F/NkT of the sum of the terms of second and higher order. It amounts to -0.47. The second-order term can be calculated knowing the slope of the curve of Fig. 1. A value of -0.45 is obtained. This is to say that the contribution of all the terms of an order higher than the second amounts to 0.02 only. The second-order term is equal, by the way, to

$$(\langle W\rangle_0{}^2-\langle W^2\rangle_0)/NkT\ ,$$

which can be computed in the reference system, and this offers a more direct but less precise way of evaluating it. The value -0.45 ± 0.02 is thus obtained. As a conclusion we see that the λ expansion is converging very rapidly in the dense liquid region where the convergence ratio is of the order of $\frac{1}{15}$. It is therefore a legitimate expansion to use in the case of liquids. This result is significant from a theoretical standpoint. Practically the problem is still not trivial, because, if quantitative results are to be derived, it is necessary to evaluate with care both the first- and second-order terms.

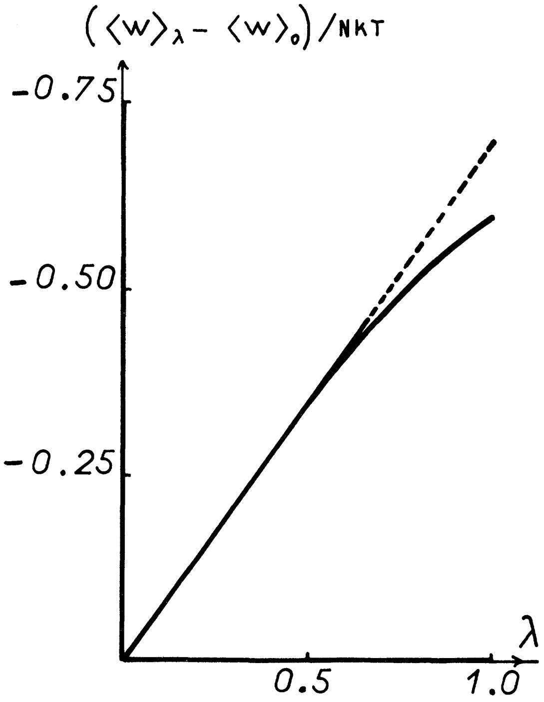

FIG. 1. Results of the direct Monte Carlo computation of $\langle W\rangle_\lambda/NkT$.

III. TREATMENT OF THE REFERENCE SYSTEM

For the pressure of the equivalent hard-sphere gas we use an expression that uses the known virial coefficients[8] and fits the computer results[9] at high density:

$$\frac{p}{\rho kT}=1+\sum_{n=1}^{\infty} a_n \rho'^n \ , \qquad (4)$$

with $\rho'=2\pi\rho d^3/3$; $a_1=1$, $a_2=0.625$, $a_3=0.286\,95$, $a_4=0.1103$, $a_5=0.0386$, $a_6=0.0138$, $a_8=0.004\,334$, $a_{13}=0.3093\times10^{-4}$, and all the other a_n are taken to be zero.

In Table I, we compare the results obtained using the Barker-Henderson approximation (3) for d with those of the reference system at the temperature $T=1.35$ (reduced units, i.e., $\sigma=\epsilon/k=1$, are used throughout). For $\rho\leqslant 0.3$, the Percus-Yevick (PY) equation was used, and at higher densities (up to $\rho=0.8$) the results were obtained by a standard Monte Carlo calculation (864 particles, 350×864 equilibrium configurations). The agreement for the pressure and free energies is seen to be excellent. We give also a comparison for a point at a lower temperature, not far from the triple point. At $\rho=0.85$, $T=0.72$, $(p/\rho kT)_0=7.78\pm0.05$. For the same state we obtain, using (2) and (4), the value 7.67. The approximation is as good as could be wished.

As we have said in the introduction, Barker and Henderson evaluate the first-order term by replacing the radial distribution function for the reference system $g_0(r)$ by that corresponding to hard spheres of diameter d in the PY approximation. An indirect by instructive test of the validity of this approximation is obtained by fitting the structure factor, i.e., the Fourier transform of the correlation function $g_0(r)-1$, with the help of the hard-sphere model studied by Verlet.[10] This model is a variant of the one introduced by Ashkroft and Lekner[11]: It consists in equating the height of the first maximum of the structure factor of a fluid at the density ρ with that of a hard-sphere gas of packing fraction η. The diameter a of the hard-sphere gas is obtained if it is required that its density $6\eta/\pi a^3$ coincide with the density ρ of the fluid. For $\rho=0.8$ and $T=1.35$, $d=0.967$. a is equal to 0.961 if the Wertheim-Thiele solution[12] is used, but a value of 0.966 is obtained for this quantity if the exact solution for the hard-sphere gas is used instead.[13] In the same way for $\rho=0.85$ and $T=0.72$, $d=0.979$. $a=0.968$ when the PY equation is used and $a=0.978$ when the hard-sphere problem is solved exactly.

The first-order contribution to F/NkT is

$$\langle W\rangle_0/NkT=\tfrac{1}{2}\beta\rho\int d\vec{r}\, g_0(r)w(r) \ .$$

In its evaluation by Barker and Henderson $g_0(r)$ is replaced by the Percus-Yevick solution for the hard-sphere system of diameter d. This replacement leads to an error which is small, but not negligible. For $\rho=0.8$ and $T=1.35$, the first-order term is equal to -3.83 when calculated exactly and to -3.89 when the hard-sphere approximation is used. For $\rho=0.85$ and $T=0.72$, $\langle W\rangle_0/NkT=-7.79$ and its approximate value is -7.95. This discrepancy is due partly to the use of the hard-sphere model, partly to its treatment through the PY approximation: If the real reference system is calculated in the PY approximation and the results compared with the exact ones, the effect of using this approximation is evaluated. We thus find -3.85 and -7.84 for $\langle W\rangle_0/NkT$ in the two cases studied above.

We have just shown that the error made by Barker and Henderson on the first-order term is rather small. It will be seen below, however,

TABLE I. Monte Carlo and approximate results on the $T=1.35$ isotherm. "Exact" compressibility factor, column 2, and free energy, column 3, both for the reference system. Column 4: excess free energy correct up to the first order in λ. Column 5: "exact" values of the excess free energy obtained by using the data of Table II. Column 6: values of the sum of the higher-order correction terms. Compressibility factor, column 7, and excess free energy, column 8, for the reference system obtained using the Barker and Henderson expression (3) for the temperature-dependent diameter. Column 9: excess free energy obtained from the equation of state (7). Column 10: second-order correction term in the "macroscopic compressibility" approximation.

	Exact calculation					Approximate calculation			
ρ	$\frac{p_0}{\rho kT}$	$\frac{F_0}{NkT}$	$\frac{F_1}{NkT}$	$\frac{F_1}{NkT}$	$\frac{F_i-F_1}{NkT}$	$\frac{p_0}{\rho kT}$	$\frac{F_0}{NkT}$	$\frac{F_i}{NkT}$	m.c. correction term
0.1	1.21	0.204	−0.226	−0.295	−0.069	1.21	0.201	−0.299	−0.052
0.2	1.48	0.430	−0.444	−0.562	−0.118	1.49	0.429	−0.573	−0.075
0.3	1.82	0.690	−0.673	−0.796	−0.123	1.84	0.689	−0.816	−0.082
0.4	2.31	0.991	−0.874	−0.998	−0.124	2.29	0.989	−1.024	−0.080
0.5	2.89	1.343	−1.040	−1.159	−0.119	2.88	1.336	−1.186	−0.072
0.6	3.68	1.755	−1.124	−1.258	−0.134	3.65	1.745	−1.289	−0.063
0.7	4.67	2.237	−1.145	−1.289	−0.144	4.70	2.229	−1.310	−0.051
0.8	6.07	2.814	−1.019	−1.190	−0.171	6.12	2.811	−1.210	−0.040

that the second-order terms are not much larger than this error.

IV. ON BARKER'S EVALUATION OF THE SECOND-ORDER TERM

Barker and Henderson have proposed two approximations for the second-order term, which they show to give very similar results. We present here the results yielded by one of these, the so-called "macroscopic compressibility" approximation. The second-order term is then simply replaced by

$$\rho \int d\vec{r}\, w^2(r) g_0(r)/(\partial p/\partial \rho)_0 \ .$$

In Table I we give results concerning the isotherm $T = 1.35$, which is very near the critical isotherm of the Lennard-Jones potential. The exact free energy is obtained (column 5) by integrating $p/\rho kT$ along the isotherm: The excess part of the free energy is given by

$$F_i/NkT = \int_0^{\rho} (p/\rho kT - 1) d\rho/\rho \ . \qquad (5)$$

The equation of state was obtained from the PY II equation[14] when $\rho \leq 0.30$ and through Monte Carlo calculations, the results of which are given in Tables II and III, from $\rho = 0.35$ to $\rho = 0.80$. The reference system is treated by the PY equation for $\rho \leq 0.3$ and by the Monte Carlo method at higher densities. We thus obtain F_0/NkT (column 3).

We then calculate the first-order contribution $\langle W \rangle_0/NkT$ to the free energy. In column 4 we give F_1/NkT, where F_1 is the free energy calculated to the first order in the λ expansion. $(F_i - F_1)/NkT$ is the sum of higher-order terms. It is given in column 6. It is seen that the ratio of that term to the first-order term is decreasing when the density increases: The λ expansion is most satisfactory at high density. The Barker and Henderson approximation for the second-order term is given in column 10. We see that the correction term thus calculated, although of the correct sign and of the right order of magnitude, is quantitatively incorrect, especially so at high density. For instance, for $\rho = 0.8$, the correction term found using the "macroscopic compressibility" formula is -0.040, when the correct value for $(F - F_1)/NkT$ is -0.171. We may recall, however, that an error of -0.06 is made if the first-order term is evaluated using the hard-sphere approximation. If we use the Barker and Henderson method both for the second- and the first-order term we find an apparent correction term of -0.10.

For $T = 0.72$ and $\rho = 0.85$ we know that the second-order term is equal to -0.45. Using the Barker and Henderson approximation, a value of -0.14 is found. This is, in magnitude, three times too small. On the other hand, the error on the first-order term, evaluated in the hard-sphere approximation, is -0.16. The apparent second-order term is then -0.30 nearer to the exact value -0.45.

V. EQUATIONS OF STATE FOR THE LENNARD-JONES FLUID

We shall now try to use the λ expansion as a guide in order to write down semiempirical equations of state, first for the Lennard-Jones fluid and then for real ones. A possible way to do this is to derive an equation of state from the following approximation for the free energy

$$F/NkT = F_0/NkT + \beta\psi_1(\rho) + \beta^2\psi_2(\rho) \ , \qquad (6)$$

where the first term is the equivalent hard-sphere (hs) free energy defined above. The dependence on temperature of the first-order term

TABLE II. $p/\rho kT$ as a function of the density for the isotherm $T = 1.35$. Column 2: Monte Carlo results. Column 3: results obtained using the PY II equation (Ref. 14). Column 4: equation of state (7). Column 5: equation of state (11).

ρ	MC	PY II	Eq. (7)	Eq. (11)
0.3	0.35	0.36	0.32	0.37
0.35	0.30	0.31	0.27	0.31
0.4	0.27	0.27	0.25	0.28
0.5	0.30	0.30	0.32	0.32
0.55	0.41	0.45	0.42	0.41
0.7	1.17		1.22	1.22
0.8	2.42		2.41	2.42
0.9	4.58		4.57	4.54
0.95	6.32		6.25	6.37

TABLE III. The excess internal energy per particle U_i/N as a function of the density for the isotherm $T = 1.35$. Column 2: Monte Carlo results. Column 3: results obtained using the PY II equation. Column 4: internal energies according to the equations of state (7). Column 5: the same with equation of state (11).

ρ	MC	PY II	Eq. (7)	Eq. (11)
0.3	−2.09	−2.18	−1.99	−2.05
0.35	−2.40	−2.47	−2.31	−2.38
0.4	−2.75	−2.77	−2.65	−2.72
0.5	−3.37	−3.36	−3.31	−3.38
0.55	−3.70	−3.66	−3.64	−3.70
0.7	−4.68		−4.60	−4.67
0.8	−5.25		−5.18	−5.22
0.9	−5.66		−5.60	−5.65
0.95	−5.71		−5.69	−5.71

in the λ expansion of F/N is due only to the temperature dependence of the reference system and is expected to be weak. $\psi_1(\rho)$ is the temperature-independent part of that first-order term. A linear approximation for the β-dependent part of that term and the temperature-independent part of the second term are lumped together in $\psi_2(\rho)$ which is supposed to be, and so it turns out, an order of magnitude smaller than $\psi_1(\rho)$. From (6) follows the equation of state

$$p/\rho kT = (p/\rho kT)_{\text{hs}} + \beta\rho\psi_1'(\rho) + \beta^2\rho\psi_2'(\rho) \quad . \tag{7}$$

We expand $\psi_1(\rho)$ and $\psi_2(\rho)$ in the density

$$\psi_1(\rho) = \sum_1^\infty b_n \frac{\rho^n}{n} \;, \quad \psi_2(\rho) = \sum_1^\infty c_n \frac{\rho^n}{n} \; . \tag{8}$$

If van der Waals's theory were correct we would have

$$b_1 = \tfrac{1}{2}\int d\vec{r}\, w(r) = -16\pi/9 = -5.59 \tag{9}$$

and all other b's and c's equal to zero. We shall need a more complicated form for ψ_1 and ψ_2 to fit the equation of state with the results from machine computation (see Verlet[15] and the Appendix). The value of b_1 so obtained turns out to be of the same order of magnitude as the one given by van der Waals's theory.

With five parameters we can obtain a fit for $p/\rho kT$ with an average error of the order of 0.02. Adding more parameters does not improve the fit appreciably. The error is systematic at low density, where the equation of state is not expected to work very well, but is of the order of the statistical error at high density. The excess internal energy is given by

$$\frac{U_i}{N} = \frac{3d'_\beta}{d}\left[\left(\frac{p}{\rho kT}\right)_{\text{hs}} - 1\right] + \psi_1(\rho) + 2\beta\psi_2(\rho). \tag{10}$$

In order to obtain a good fit for this quantity we must add one more parameter in $\psi_2(\rho)$. The error on the internal energy is then always less than 0.1. The parameters obtained through this fit are

$$b_1 = -6.639, \quad b_7 = 4.458, \quad b_{13} = -4.024 \;,$$
$$c_1 = -0.127, \quad c_3 = -1.362, \quad c_{14} = 5.586 \; .$$

A comment should be added on the fitting procedure: As we do not *a priori* expect the equation of state to be valid when both the temperature and the density are low, we have excluded, when making the fit, all points for which both T is smaller than 1.6 and ρ is smaller than 0.5. If we nevertheless try to obtain the critical point from the equation of state (7), we obtain

$$T_c = 1.37, \quad \rho_c = 0.31, \quad \beta_c p_c/\rho_c = 0.32 \quad .$$

The critical constants for the Lennard-Jones potential were obtained in Ref. 14 using the PY II equation. The validity of this equation can be appreciated from the new data presented in Table II. The critical constants of the Lennard-Jones potential (in a situation where the one-particle density is not allowed to vary spatially, see Sec. VII) are thus found to be

$$T_c = 1.36 \pm 0.03, \quad \rho_c = 0.36 \pm 0.03,$$
$$\beta_c p_c/\rho_c = 0.31 \pm 0.04 \quad .$$

The agreement is surprisingly good.

The addition of a term of the form $\beta^3\psi_3(\rho)$ does not seem to improve the equation of state. A better agreement with the data to be fitted would require probably the use of full high-order polynomial representations for $\psi_1(\rho)$ and $\psi_2(\rho)$ instead of the "lacunar" polynomials that we have used for the sake of simplicity.

We have used also another form of the equation of state that is more suited to very high temperature where ρ can become large, but where ρd^3 stays smaller than unity. For this we remark that the first term in β may be viewed as an approximation for $\rho\int w(r/\sigma)g_0(r/d, \rho d^3)d\vec{r}$, where $g_0(r/d, \rho d^3)$ is the radial distribution function of hard spheres of diameter d for the density ρd^3. As d is a slowly varying function of β, the first term may be replaced by $\beta\Phi_1(\rho d^3)$, where Φ_1 is a function to be determined. The leading correction will be taken, as above, as a part of a β^2 term.

The equation of state is thus written as

$$p/\rho kT = (p/\rho kT)_{\text{hs}} + \beta\rho d^3\Phi_1'(\rho d^3) + \beta^2(\rho d^3)^2\Phi_2'(\rho d^3) \quad . \tag{11}$$

The expression for the excess internal energy is slightly modified into

$$\frac{U_i}{N} = 3\frac{d'_\beta}{d}\; \frac{p}{\rho kT} - 1 \; + \Phi_1(\rho d^3) + 2\beta\Phi_2(\rho d^3) \quad . \tag{12}$$

$\Phi_1(\rho d^3)$ and $\Phi_2(\rho d^3)$ will again be expanded as

$$\Phi_1(\rho d^3) = \sum_1^\infty b_n'(\rho d^3)^n/n \quad ,$$

$$\Phi_2(\rho d^3) = \sum_1^\infty c_n'(\rho d^3)^n/n \quad . \tag{13}$$

A fit slightly better than for the equation of state (7) is obtained with the following values for the parameters:

$$b_1' = -5.851, \quad b_2' = -5.757, \quad b_5' = 16.239,$$
$$b_7' = -5.966, \quad b_{27}' = -81.585, \; c_1' = -1.270,$$
$$c_2' = 7.438, \quad c_3' = -8.938, \quad c_{28}' = 197.294$$

Adding more parameters does not improve the fit appreciably. With the equation of state (11) the critical constants turn out to be

$$T_c = 1.36, \quad \rho_c = 0.33, \quad \beta_c p_c/\rho_c = 0.36 \ .$$

VI. VALIDITY OF THE EQUATIONS OF STATE FOR THE LENNARD-JONES POTENTIAL

In this section, we shall give a few examples of the use of the equations of state (7) and (11) and of the degree of success that can be expected from them.

(1) On the isotherm $T = 1.35$ already mentioned, it can be seen from Table I that F_i/NkT calculated using the equation of state (7) differs by 0.03 at most from the "exact" one.

(2) In Tables II and III, we give a comparison for the pressures and internal energies on the same isotherm: the Monte Carlo results[25] obtained with the collaboration of Hansen are compared with the results from the equations of state. There is a good agreement both for the pressures and the internal energies at high densities. For low values of the densities, where the equation of state is not supposed to work very well, it is seen that the agreement is not so good. A comment should be made on the Monte Carlo results at $\rho = 0.3$ and $\rho = 0.35$. Although, for those states, the pressure was found to remain quite stable during the computation, the internal energy is uncertain as its magnitude rose continuously, and the values given in Table III are only vague indications. In our experience this situation arises when the system tends to separate into two phases, and this tends to confirm the fact that the isotherm $T = 1.35$ is slightly under-critical. We display also in the same tables the values of the thermodynamical quantities obtained with the PY II equation, because it can now be compared with more precise Monte Carlo results. Its range of validity is seen to extend up to $\rho = 0.55$, and is thus larger than we had believed before.[14]

(3) In Tables IV–VI, we give a few examples of evaluations of derivatives of thermodynamical quantities, which are expected to be more imprecise than the pressures or internal energies. The quantity $(1/\rho)\partial p/\partial T - 1$ is shown in Table IV for several values of the temperature on the isochore $\rho = 0.85$. The results of the equations of state (7) and (11), Columns 3 and 4, respectively, are compared with the "exact" values obtained through differentiation of a polynomial fit of the data given in Ref. (15) and in the Appendix. These values are slightly different from those of Lebowitz, Percus, and Verlet,[16] which were obtained graphically and which are probably less precise. We give also in Table IV, for the sake of comparison, the values of thermodynamical derivatives obtained directly in Ref. 16 in terms of the fluctuation of the product of the virial and the potential energy, which was evaluated in the molecular dynamics computations. In Table V we give the inverse compressibility $\beta(\partial p/\partial \rho)$ on the isotherm $T = 1.35$, for several values of the

TABLE IV. $(1/\rho)\partial p/\partial T - 1$ on the isochore $\rho = 0.85$. Column 2: "exact" values obtained from molecular dynamics by numerical differentiation. Column 3: values calculated from the equation of state (7). Column 4: the same with Eq. (11). Column 5: values obtained in Ref. (16) through a direct evaluation of the appropriate fluctuation.

T	"Exact"	Eq. (7)	Eq. (11)	Fluctuation
2.89	3.72	3.8	3.8	3.3
2.20	4.1	4.2	4.2	4.0
1.21	5.3	5.3	5.4	4.6
1.13	5.5	5.4	5.5	4.8
0.88	6.0	5.9	6.2	6.4

TABLE V. $\beta(\partial p/\partial \rho)$ on the isotherm $T = 1.35$. Column 2: "exact" values obtained from molecular dynamics by numerical differentiation. Column 3: values calculated from the equation of state (7). Column 4: the same with Eq. (11). Column 5: values obtained using the Ornstein-Zernike formula and the prolongation procedure for the correlation function described in Ref. (10).

ρ	"Exact"	Eq. (7)	Eq. (11)	O. Z.
0.4	0.18	0.21	0.11	0.43
0.5	1.01	1.09	0.98	1.41
0.55	1.82	1.92	1.85	2.23
0.7	7.24	7.23	7.41	8.6
0.8	15.25	15.1	15.0	16.0
0.9	30.86	30.4	30.4	30.4
0.95	44.22	43.2	51.9	

TABLE VI. The excess specific heat per particle C_V^i. Column 2: "exact" values. Column 3: values calculated from the equation of state (7). Column 4: the same with Eq. (11). Column 5: values obtained in Ref. (16) in terms of the fluctuation of the potential energy.

T	"Exact"	Eq. (7)	Eq. (11)	Fluctuation
2.89	0.66	0.65	0.73	0.59
2.20	0.79	0.72	0.78	0.78
1.21	0.97	1.02	0.95	0.84
1.13	0.98	1.08	0.99	0.78
0.88	1.03	1.41	1.15	1.24

density. The "exact" results (Column 2) are obtained by numerical differentiation of a polynomial fitting the Monte Carlo results of Table II. They are seen to agree very well with the results yielded by Eq. (7) (Column 3) and Eq. (11) (Column 4), except that in the latter case there is a discrepancy for the highest value of the density: A more complicated form of the Φ_1 and Φ_2 function would be necessary to get a better agreement. We thought it interesting to give in the same table (Column 5), the inverse compressibility obtained by applying the Ornstein-Zernike relation to the correlation function obtained from molecular dynamics computations, following the procedure described in Ref. 10. The "exact" radial distribution function is used in the small r region (including the first peak) and the Percus-Yevick equation afterwards. As expected, the agreement is fair, but not very good.

In Table VI are given examples of the excess specific heat per particle $C_V{}^i$ on the isochore $\rho = 0.85$. In Column (2) we give the results of a numerical differentiation of the energy with respect to the temperature, on the isochore. The comparison with the equation of state (7) (Column 3) is seen to lead to rather poor results at low temperature. Equation (11) (Column 4) gives substantially better results. In the last column of the table we show the specific heats obtained in Ref. 16 in terms of the fluctuations of the potential energy.

VII. EQUATION OF STATE FOR ARGON AND XENON

We have made a fit to the known experimental data for the equation of state of liquid argon and xenon. The experimental data for argon are numerous and precise. Adding together the results obtained by the Amsterdam,[17] Toronto,[18] and Princeton[19] groups, it is possible to cover a region ranging in temperature from the triple point to three times the critical point and reaching, in density, the solidification region. The data for xenon are more scarce. We have used the pressures and internal energies given by Levelt[17] for a rather narrow strip in reduced temperature, ranging from 1.35 to 1.9, the reduced densities going up to 0.85. We have also used the known[20] triple point constants of xenon. In both cases we have used as reduction parameters the Lennard-Jones potential constants ϵ and σ determined from the second virial coefficients: for argon,[21] $\epsilon/k = 119.8$, $\sigma = 3.405$ Å. For xenon[22] $\epsilon/k = 224.5$, $\sigma = 4.064$ Å. The fits have been made excluding a wide domain around the critical point, corresponding to $\rho < 0.55$ and $T < 1.8$.

As we do not know the interaction we must now choose for the temperature-dependent diameter a definite form depending on parameters that must be determined in the fitting process. We have tested in the Lennard-Jones case that $d(\beta)$ could be fitted, for $T < 5$, by an approximant of the form

$$d(\beta) = (\alpha_3 + \alpha_1\beta^{-1})/(1 + \alpha_2\beta^{-1}) \ .$$

The constants turn out to be $\alpha_1 = 0.1680$, $\alpha_2 = 0.1958$, and $\alpha_3 = 0.9955$ with an error of less than 4×10^{-4}. This entails no error in the pressure. The internal energy is unchanged except at the highest temperature in the range considered. We have only used the equation of state (7). The parameters giving the functions $\psi_1(\rho)$ and $\psi_2(\rho)$ are for argon: $b_1 = 5.627$, $b_7 = 5.945$, $b_{13} = -1.683$, $c_1 = -0.875$, $c_3 = -0.381$, $c_{14} = 0.686$. The core parameters turn out to be $\alpha_1 = 0.1479$, $\alpha_2 = 0.1727$, and $\alpha_3 = 0.9667$. The error on $p/\rho kT$ is in general smaller than 0.01, except at very high temperature where there seem to be larger discrepancies due to slight differences between various experiments. The error on the values of the internal energies given by Levelt are of the order of 0.02.

The fit for xenon is as good as for argon. But it must be emphasized again that it has been made using a much smaller set of densities and temperatures. The parameters giving the best fit are $b_1 = -4.973$, $b_7 = 9.243$, $b_{13} = -6.204$, $c_1 = -1.997$, $c_2 = 6.770$, $\alpha_3 = -8.037$, $c_{14} = 1.850$, $\alpha_1 = 0.2677$, $\alpha_2 = 0.3022$, and $\alpha_3 = 0.8969$.

We shall make a few remarks about these equations of state. We begin by discussing the temperature-dependent hard-sphere diameter $d(\beta)$. Such a diameter has already been considered by Dymond and Alder[23] in a rather similar way. These authors have determined the hard-sphere diameter in the following fashion: Let us consider, at some low inverse temperature β and for a given value of the density, the equation of state (7). If β is small enough, we can neglect the β^2 term. Let the variation with β of $(p/\rho kT)_{\text{hs}}$, which is small [as compared with $\psi_1(\rho)$], be altogether neglected. Then $(p/\rho kT)_{\text{hs}}$ can be determined by the intercept, for $\beta = 0$, of the tangent drawn to the representative curve of $p/\rho kT$ at the point corresponding to the inverse temperature β. We can therefore determine d as a function of β, using this procedure. This diameter should not depend – and does depend very little – on the value of the density for which the fit is done. The diameter so determined by Dymond and Alder differs from ours by a few percent only. This difference may be due to the approximations we have mentioned above.

As an illustration we give in Table VII the values of the diameter for a low temperature ($T = 1$) and for a high temperature ($T = 5$). From these data we would conclude that for a temperature not too high ($T < 5$), the effective two-body repulsion is, in argon, less extended and steeper than in the case of the Lennard-Jones potential. We also see from Table VII that the xenon diameter is substantially smaller than that of argon. We should note that, in the reduced units for xenon that we have used, the density for the triple point of xenon turns out to be 0.951 when the triple-point density of argon is 0.839. In order to obtain the same reduced density at the triple point for xenon as for argon, we should multiply the unit of length by 1.042. It is seen that this has the effect of reducing very much the discrepancy between the argon and xenon entries in Table VII. In other words we would conclude that xenon has a core 4% larger than indicated by the fit to second virial coefficient.

TABLE VII. The equivalent hard-sphere diameter $d(\beta)$ of argon and xenon for two values of the inverse temperature β in the case of the Lennard-Jones potential. The diameters are expressed in units of σ, where for argon (Ref. 21) $\sigma = 3.405$ Å, and for xenon (Ref. 22) $\sigma = 4.064$ Å.

β	L. J.	Ar	Xe
1	0.973	0.939	0.894
0.2	0.927	0.917	0.890

As we have shown the ability of the equation of state (7) to predict the critical temperature in the Lennard-Jones case – it was overestimated by only 0.01 – we may calculate the same quantity in the case of argon. We find for the critical temperature the value 1.35 instead of the 1.26 found experimentally. The explanation for most of this very large discrepancy seems to us to lie in the following: The equation of state is a straight expansion in the inverse temperature and the density, and does not allow for the singularities characteristic of the critical point. It is not surprising that in the Lennard-Jones case it agrees with the molecular dynamics computation, which does not allow for large scale density variations. The same is true with the PY II equation where the one-body correlation function is kept constant as in the usual integral equations.[24] All of these approaches are consistent with the classical van der Waals view on the critical point. As is well known, the situation is different in nature where large scale density variations do occur. They are responsible for the well-known flattening of the ρ versus T coexistence curve. A consequence of these effects is a reduction of the critical temperature amounting, as we see by the preceding argument, to about 6%.

VIII. CONCLUSION

The excellence of the Barker-Henderson expression for the equivalent hard-sphere diameter, as well as the rapid convergence of the λ expansion, have enabled us to write down semiempirical equations of state for liquids and dense gases. These equations have been derived in the case of the Lennard-Jones fluid, and for argon and xenon. Improvements in these equations of state, as well as their extension to other simple fluids, will be carried out.

The considerations given in the present paper can be extended to the case of solids at temperatures which are not too low. The theory of melting which results, as well as the vaporization curves obtained from the equation of states given here, will be published in a later paper.[25]

IX. ACKNOWLEDGMENT

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APPENDIX

We present here some new data which have been used in conjunction with those of Ref. (15) in fitting the equations of state of the Lennard-Jones fluid. Using the equations of state as a tool we also review the computations made so far in that case.

In the first part of Table VIII we give some Monte Carlo results on the isotherm $T = 2.74$ in collaboration with Hansen using a 864-particle system and of about 4×10^5 configurations. In the second part of the table we give a number of new molecular dynamics results obtained by the method of Ref. 15. In the last part of the table we give a number of points of Ref. 15 that must be corrected either for misprints or for slight errors.

To these data should be added those presented in Tables II and III for the isotherm $T = 1.35$, which supersede the 108-particle Monte Carlo results of Ref. 14. Those points are compatible with the newer ones but less precise.

The agreement of the equation of state with the two higher density isochores, given by McDonald and Singer[26] who used a 32-particle system and the Monte Carlo method, is quite good. It would be better still if their value of $p/\rho kT$ were raised by 0.04. A similar conclusion can be drawn concerning the points of the isotherm $T = 1.0579$ obtained by Wood[27] using a 32-particle system and the Monte Carlo method, with the exception of the highest density point. There a disagreement appears. For $\rho = 0.833$, Wood finds $p/\rho kT = 1.99$ when the equation of state (7) yields for the same quantity the value 2.13.

The agreement is also within the expected accuracy for the old $T = 2.74$ isotherm of Wood and Parker[28] except, again, at high density. For $\rho = 1$, for instance, the new Monte Carlo result of Table VIII is $p/\rho kT = 7.44$. Wood and Parker obtained 7.06 for the same quantity.

The computations made by Fickett and Wood[29] at very high temperature (32 particles, Monte Carlo method) require a more careful investigation. There the equation of state (11) should be used. Let us first consider their points at very high temperature ($T = 100$). The β term in the equation of state is practically negligible as may be seen from Table IX. The hard-sphere equation of state is then practically valid. We see that the Monte Carlo compressibility factor for $\rho = 1$ is a little low when compared with the one given by the equation of state. This tendency is more marked for the $\rho = 2$ point. The two points at $\rho = 2.5$ and $\rho = 3.33$ are probably deep in the metastable region. The Monte Carlo pressures are being compared with what may be unduly long extrapolations of the equation of state for hard spheres: nevertheless the values seem to be surprisingly different. The points at $T = 20$, except one, and all the points at $T = 5$ are in the stable fluid region. It is seen that for $\rho < 1$ the agreement with the equation of state (11) is good and that when $\rho \geqslant 1$ the pressure given by Fickett and Wood is substantially lower than the one given by the equation of state. The question is whether this may not be due to an inadequacy of the Barker-Henderson approximation for high values

TABLE VIII. Compressibility factors and excess internal energies as a function of density and temperature. (a) First group of states: Monte Carlo results. (b) Second group of states: molecular dynamics results. (c) Third group of states: revised data of Ref. (15).

ρ	T	$\beta p/\rho$	U_i
(a) 0.55	2.74	1.65	−3.21
0.75	2.74	2.64	−3.90
0.9	2.74	5.14	−4.41
1.00	2.74	7.39	−4.18
1.08	2.74	9.59	−3.80
(b) 0.35	1.363	0.35	−2.40
0.65	1.43	0.98	−4.31
0.65	1.83	1.56	−4.12
0.65	3.67	2.46	−3.32
0.75	1.12	1.04	−5.13
0.75	1.30	1.60	−5.00
0.75	2.040	2.68	−4.52
0.85	0.72	0.43	−6.22
0.85	0.76	0.82	−6.07
0.85	1.273	3.17	−5.55
0.85	2.145	3.06	−4.80
(c) 0.45	1.552	0.57	−2.98
0.5	1.36	0.32	−3.38
0.5426	1.326	0.37	−0.36
0.5426	1.404	0.48	−3.63
0.5426	3.26	1.81	−3.00
0.85	0.591	−1.20	−6.46
0.85	0.658	−0.20	−6.39
0.88	0.94	2.77	−6.04
0.88	1.095	3.48	−5.85

TABLE IX. High-temperature equation of state of the Lennard-Jones fluid. Column 3: value of ρd^3 calculated using (3). Column 4: compressibility factor obtained by Fickett and Wood Ref. 29 using 32 particles and the Monte Carlo method. Column 5: results obtained with the equation of state (11). Column 6: hard-sphere compressibility factor.

				$p/\rho kT$	
T	ρ	ρd^3	W.F.	Eq. (11)	hs
100	0.5	0.24	1.67	1.69	1.70
100	1	0.48	2.95	3.06	3.10
100	2	0.96	9.50	13.00	13.29
100	2.5	1.2	16.29		(35.6)
100	3.333	1.6	27.85		(346)
20	0.5	0.326	1.89	1.97	2.10
20	0.667	0.435	2.51	2.59	2.75
20	1.000	0.65	4.46	4.74	4.97
20	1.333	0.87	8.00	9.43	9.69
20	2.000	1.30	20.30		(60.0)
5	0.5	0.40	1.87	1.90	2.51
5	0.667	0.53	2.63	2.79	3.56
5	1.00	0.80	6.34	6.78	7.70

of the temperature and density. That this is indeed the case is shown by the following example. For $\rho = 2$, $T = 100$, a direct Monte Carlo computation agrees quite well with that of Fickett and Wood: A value of 9.2 is obtained for $p/\rho kT$ when Fickett and Wood give the value 9.5. This is in strong disagreement with the results obtained from Barker and Henderson's theory.

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Correlation Length of Density Fluctuations in Liquids

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It is shown that in a liquid whose bulk modulus relaxes with relaxation time τ', there exist density fluctuations whose correlation length is approximately $v\tau'/\pi$, where v is the sound velocity at $\Omega_0 = (\tau')^{-1}$.

It has been suggested that one might study the correlation function of density fluctuations in a liquid by measuring the correlation function of the scattered light.[1] For this to be possible it is of course necessary that the correlation length in the liquid be comparable to the wavelength of the incident light. In the case of Rayleigh scattering near the critical point it is well known that the