GENERALIZED VAN DER WAALS THEORY

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(Recibido: marzo 9, 1975)

ABSTRACT: Within the spirit of the standard mean-field, van der Waals equation of state theory, asymptotically exact for low densities and high temperatures (when realistic potentials are used), we give an ***exact*** extension to all temperatures in terms of confluent hypergeometric functions as well as a ***partial*** extension, coming from the repulsive portion of the interaction, to higher densities, for the Sutherland potential.

In the usual[1] "mean-field" derivation of the van der Waals equation of state for fluids of N particles in a volume V interacting via an infinitely-repulsive core of diameter σ plus some attractive tail $v_{att}(r)$, one starts with the independent particle partition function

$$Z = \mathcal{Q}^N/N!\,, \quad \mathcal{Q} = \Lambda^{-3}(V-Nb)\exp(-U/2kT)\,, \quad \Lambda \equiv (2\pi\hbar^2/mkT)^{\frac{1}{2}} \qquad (1)$$

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* Fellow of the Mexican-Italian Exchange Program sponsored by the Consejo Nacional de Ciencia y Tecnología.

** Work partially supported by the Instituto Nacional de Energía Nuclear (México).

where the "excluded volume per particle" b is taken by van der Waals as the constant $2\pi\sigma^3/3$ and the "mean attractive field", calculated self-consistently with (1), is

$$U = 4\pi\rho\int_{\sigma}^{\infty} dr\, r^2\, v_{att}(r) \equiv -2\rho a\,, \tag{2}$$

where the constants a and b are independent both of density ρ and temperature T. The relations for Helmholtz free energy F and pressure P

$$F = -kT\ln Z, \quad P = -(\partial F/\partial V)_{NT} \tag{3}$$

then lead at once to the celebrated equation

$$P/kT = \rho/(1-b\rho) - (a/kT)\rho^2 \xrightarrow[b\rho<<1]{} \rho + [b-a/kT]\,\rho^2 + b^2\rho^3 + b^3\rho^4 + \ldots \tag{4}$$

where the last member explicitly displays the associated virial expansion, the quantity in brackets being the predicted second virial coefficient.

However, the *exact* such coefficient is really

$$B_2(T) = \tfrac{2}{3}\pi\sigma^3 - 2\pi\int_{\sigma}^{\infty} dr\, r^2\,\{\,[\exp(-v_{att}(r)/kT)] - 1\} \tag{5}$$

and reduces to the predicted quantity only if $kT >> |v_{att}(r)|$. Hence, the "conventional" van der Waals theory, with "realistic" potential, is *exact* for i) small densities and ii) high temperatures. In spite of this apparent restrictiveness, the standard equation (4) not only possesses the "loops" characteristic of the gas-liquid phase transition below a critical temperature T_c and pressure P_c, but also gives values for the critical quantities P_c, V_c, T_c in rough agreement with experiment.[2] The quality of agreement, when compared with that of typical "cell"[3] and "hole"[4] theories[5] of liquids is, in general, not worse.

The question arises whether one can relax restrictions (i) and (ii) above, while maintaining the (mean-field) spirit of the van der Waals theory, to obtain, e.g., an improved *location* of the critical point, albeit not, of course, its *detailed behaviour*. Some initial results towards answering this question, for the Surtherland potential, are given in this paper by lifting (ii) completely but (i) only partially.

1. *Extension to all temperatures*. Relaxing the *high-temperature restriction* involves evaluating the full contribution from the exponential in (5), which leads to a temperature-dependent coefficient. For concreteness, we take for the attractive tail

$$v_{att}(r) = -\epsilon(\sigma/r)^6 \qquad (r > \sigma; \epsilon > 0). \tag{6}$$

Then, the integral in (5), as far as we know, previously only expressible as a slowly-convergent infinite series, can be done analytically by parts, since

$$\begin{aligned} &-2\pi \int_\sigma^\infty dr\, r^2 \{[\exp(\epsilon/\boldsymbol{k}T)(\sigma/r)^6] - 1\} \\ &= {}^2\!/\!_3\, \pi\sigma^3 \{[\exp(\epsilon/\boldsymbol{k}T)] - (\epsilon/\boldsymbol{k}T) \int_0^1 dy y^{-1/2} [\exp(\epsilon y/\boldsymbol{k}T)]\} \\ &= {}^2\!/\!_3\, \pi\sigma^3 \{[\exp(\epsilon/\boldsymbol{k}T)] - 2(\epsilon/\boldsymbol{k}T)\, {}_1F_1(1/2, 3/2; \epsilon/\boldsymbol{k}T)\} \end{aligned} \tag{7}$$

where ${}_1F_1$ is the confluent hypergeometric function.[6] Using well-known recursion relations,[6] the exact second virial coefficient for the (Sutherland) potential reduces to

$$\begin{aligned} &B_2(T) = {}^2\!/\!_3\, \pi\sigma^3\, {}_1F_1(-1/2, 1/2; \epsilon/\boldsymbol{k}T) \equiv b - a(T)/\boldsymbol{k}T \\ &\xrightarrow[\epsilon/\boldsymbol{k}T \ll 1]{} b - a/\boldsymbol{k}T + O[(\epsilon/\boldsymbol{k}T)^2], \end{aligned} \tag{8}$$

where we note that contributions from infinite order perturbation theory[7] are included. Substituting the van der Waals constant a in (4) by $a(T)$, and seeking the highest $T \equiv T_c$ for which $\partial P/\partial\rho = 0$, one obtains, if $x \equiv \rho/\rho_0$ where $\rho_0 \equiv \sqrt{2}/\sigma^3$ (close-packing density) and $\alpha \equiv 2\sqrt{2}\pi/3$,

$$x^{-1}(1-\alpha x)^{-2} = 2\alpha[1 - {}_1F_1(-1/2, 1/2; \epsilon/\boldsymbol{k}T_c)], \tag{9}$$

the solution of which gives

$$x_c = (3\alpha)^{-1} \tag{10}$$

$${}_1F_1(-1/2, 1/2; \epsilon/\boldsymbol{k}T_c) = -19/8 \Longrightarrow \boldsymbol{k}T_c/\epsilon = 0.470538 \tag{11}$$

$$P_c\sigma^3/\epsilon = 0.02083, \tag{12}$$

the last result following from (10), (11) and $P_c/\rho_c\boldsymbol{k}T_c = 3/8$. The latter value depends only on the density dependence of the equation of state, which being unaltered with respect to the "conventional" equation, remains the same. A marked improvement in both critical temperature and pressure is appreciated in Table I, over the conventional results.

TABLE I

Critical observables (pressure P_c, density ρ_c and temperature T_c) of gas-liquid system reduced in terms of Sutherland potential depth ϵ and hard-core radius σ (adjusted to experimental second virial coefficient). Experimental values represent average for Ar, Kr and Xe. Last two rows refer to Lennard-Jones 6-12 potential and to experimental quantities related to Ar.

	$P_c\sigma^3/\epsilon$	$(\rho_c\sigma^3)^{-1}$	kT_c/ϵ	$P_c/\rho_c kT_c$
Experimental, Ref. 2	0.027	5.022	0.471	0.291
"Conventional" van der Waals	0.018	6.283	0.296	$0.375 = \frac{3}{8}$
Extension to all T, Sec. 1	0.028	6.283	0.471	$0.375 = \frac{3}{8}$
Plus partial extension to higher ρ's, Sec. 3	0.049	4.023	0.551	0.359
Experimental, Ref. 12	0.117	3.165	1.26	0.293
Virial with first five coefficients of L-J 6-12 potential, Ref. 14	0.119	3.829	1.291	0.352

2. *Heat capacity*. The resulting heat capacity $C_V(T)$ for $T > T_c$ no longer equals the ideal gas value $(\frac{3}{2})Nk$, as predicted by the conventional theory, but is now seen from (8) to give, for $\rho = \rho_c$,

$$C_V/Nk - \tfrac{3}{2} = (\rho_c T/k)\,(\partial^2 a(T)/\partial T^2)_V = \tfrac{1}{3}\, a x_c (\epsilon/kT)^2 \; {}_1F_1(\tfrac{3}{2}, \tfrac{5}{2}; \epsilon/kT) \tag{13}$$

where serveral other recursion relations[6] have been employed to simplify the last step. The result (13) is positive and monotonic-decreasing with T.[8] The appearance of a "tail" in $C_V(T)$ for $T > T_c$ can be interpreted as coming from a non-constant pair-distribution function for $r > \sigma$, i.e., as the presence of some "short-range order".

3. ***Partial extension to higher densities.*** This is accomplished by using a density-dependent $b(\rho)$-coefficient which will reproduce correctly some higher-order virial coefficients for the *repulsive* part of the potential only. The equation of state is then

$$\pi(x) \equiv P/\rho_0 kT, \quad x \equiv \rho/\rho_0 .$$

$$\pi(x) = \pi_{bs}(x) - \alpha\,[1 - {}_1F_1(-\tfrac{1}{2}, \tfrac{1}{2}; \epsilon/kT)]\, x^2 \tag{14}$$

where the hard-sphere equation is

$$\pi_{bs}(x) = (x + x^3 b'(x))/(1 - xb(x)), \; xb(x) \equiv \rho b(\rho) \tag{15}$$

and, if B_n^{bs} is the nth hard-sphere virial coefficient,

$$xb(x) = 1 - \exp\{-\sum_{n=2}^{\infty} [\rho_0^{n-1} B_n^{bs}/(n-1)]\, x^{n-1}\}$$

$$\doteq 1 - \exp\{-\alpha x\,[(1 - a_1 x + a_2 x^2)/(1 - b_1 x + b_2 x^2)]\} . \tag{16}$$

The first equality is an *exact* relationship and the last member contains a [3,3] Padé representation based on the first six hard-sphere virial coefficients,[9] the numerical coefficients coinciding with those in Ref. 10. The $\pi_{bs}(x)$ resulting from (15) is then

$$\pi_{bs}(x) = x + \alpha x^2\,[(1 - 0.656078\,x + 0.172328\,x^2 - 0.103207\,x^3 + 0.014918\,x^4) \times$$

$$\times (1 - 2.507279\,x + 2.296418\,x^2 - 0.908646\,x^3 + 0.131336\,x^4)^{-1}] . \tag{17}$$

The hard-sphere representations (16) and (17) reproduce quite well the computer equation of state for the hard-sphere fluid, as well as accurately predict[11] the fluid-solid transition parameters. The left hand side of (9) is now replaced by $\pi'_{bs}(x)/x$, which is also found to have one and only one minimum at $x_c = 0.17575$, which in turn gives the critical temperature and pressure listed in Table I. As expected, density and compressibility tatio have improved, but at the cost of pressure and temperature agreement previously had, the recuperation of which may require including attractions, via higher virial coefficients (to our knowledge not yet available for the interaction used here, with the exception of the third one[13]), in the extension to higher densities discussed here, and will be reported later.

A suggestion of the kind of agreement which may be expected then is seen in the last two rows of Table I, where results[14] based on the first five virial coefficients of the Lennard-Jones 6-12 potential are given.

We thank T. A. Brody for providing the sub-routine to evaluate the ${}_1F_1$'s.

REFERENCES

1. T. L. Hill, ***Statistical Thermodynamics*** (Addison-Wesley, Reading, Mass., 1960), p. 286 and F. Reif, ***Statistical and Thermal Physics*** (McGraw-Hill, New York, 1965), p. 426.
2. R.C. Reid and T.K. Sherwood, *Properties of Gases and Liquids* (McGraw-Hill, New York, 1966), 2nd ed.; A. E. Sherwood and J.M. Prausnitz, J. Chem. Phys. 41 (1964) 429.
3. J.E. Lennard-Jones and A.F. Devonshire, Proc. Roy. Soc. A163 (1937) 53.
4. F. Cernuschi and H. Eyring, J. Chem. Phys. 7 (1939) 547.
5. J.M.H. Levelt and E.G.D. Cohen, in ***Studies in Statistical Mechanics***, *Vol. II*, edited by J. de Boer and G.E. Uhlenbeck (North-Holland, Amsterdam, 1964).
6. M. Abramowitz and I. Stegun, editors, *Handbook of Mathematical Functions*, (Dover, New York, 1965).
7. D. Henderson and J.A. Barker in *Physical Chemistry*, edited by H. Eyring *et al.* (Academic, New York, 1971) p. 377.
8. D. Levi and M. de Llano, J. Chem. Phys. 63 (1975) 4561.
9. F.H. Ree and W.G. Hoover, J. Chem. Phys. 40 (1964) 939.
10. W.G. Hoover and F.H. Ree, J. Chem. Phys. 49 (1968) 3609.
11. M. de Llano and S. Ramírez, J. Chem. Phys. 62 (1975) 4243.
12. J.S. Rowlinson, *Liquids and Liquid Mixtures* (Butterworths, London, 1959).
13. H.W. Graben and R.D. Present, Rev. Mod. Phys. 36 (1964) 1025.
14. J. A. Barker, P.J. Leonard and A. Pompe, J. Chem. Phys. 44 (1966) 4206; M. de Llano and A. Nava-Jaimes, Mol. Phys. (to be published).

RESUMEN

Dentro del marco general de la teoría de campo-medio de van der Waals para la ecuación de estado de un fluído, teoría que es asintóticamente exacta para bajas densidades y altas temperaturas (cuando se emplean potenciales realistas), damos una extensión *exacta* para toda temperatura, en términos de funciones hipergeométricas confluentes, así como una extensión parcial, proveniente de la parte repulsiva de la interacción, para densidades mayores, todo para el potencial de Sutherland.