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Abstract. A new method is presented for summation of the virial equation of state up to infinity. The method is based on Holleran's unit compressibility law, and leads to a new expression for the equation of state, which has promise for the prediction of the first order phase transition.

1. Introduction

The virial expansion is the most promising description of the behaviour of gases at the present time. Here the virial expansion for the equation of state is the most frequently investigated kind of expansion. The virial equation of state expresses the compressibility factor as a power series in the density, the coefficient of the $(n-1)$th power of the density being called the nth virial coefficient. The virial coefficients for a given substance are functions of temperature only. The experimental measurements of the virial cofficients, and their temperature dependence, nowadays form a most complete set of data concerning the behaviour of gases.

On the other hand, the theoretical calculation of the virial coefficients is one of the most advanced theoretical investigations of the properties of gases.

However, it is well known that the virial equations of state (and virial expansions in general) are hampered even for moderately high densities, because high order virial coefficients are needed, which cannot be calculated at the present time. Thus, the truncation of the virial series is usually made after an appropriate term, the number of which depends upon the form of intermolecular potential used in the theoretical calculations.

The problem which remains is one of summing the virial expansion through all terms, up to infinity. It was generally assumed that such a sum should not only describe the high density behaviour of gases, but also provide promise, for predicting phase transitions.

Many of the theoretical methods which have been developed to describe the high density behaviour of gases may be regarded as procedures of summation to infinity, by taking into account only some parts of the virial coefficients. We may recall here the comparatively large success of some of the approximation methods, in particular of the Percus and Yevick (1958), and hypernetted chain (Morita 1969), approximations. These approximations seem to give a fairly accurate description, but the origin of this success is not very well understood.

The most recent results along these lines have been obtained by Fuliński (1968), who has partially performed this summation, using a new graphical expansion. Later attempts

have been made by Fuliński (1970a, 1970b), to sum the virial expansion, given in the form as developed by Mayer and Ursell.

It has been found by Fuliński that the simplest stars make up the greatest contribution to the virial coefficients. The summation of the simplest stars leads to a compact equation of state, which seems to predict the existence of the first order phase transition.

In subsequent papers by Fuliński (1971), the method is extended, to sum new additional classes of graphs. One of the most interesting results found by Fuliński is the connection between some kinds of contributions from the virial coefficients, and some kinds of phase transitions.

The purpose of this paper is to present a new theoretical method of summation of the virial expansion for the equation of state. This summation is very simple and leads to an extremely simple expression, which is easy to evaluate.

2. Theory

The virial equation of state expresses the compressibility factor $Z = PV/RT$ as a power series in density $d = 1/V$:

$$Z = 1 + \sum_{n=0}^{\infty} B_n d^{(n+1)} \tag{1}$$

where B_{n-2} is the so called nth virial coefficient, which for a given substance is a function of temperature only. It has been found by Holleran (1967) that, under the condition that Z is unity, the density is a linear function of temperature, namely

$$d = d_0 \left(1 - \frac{T}{T_B} \right) \tag{2}$$

where d_0 and the Boyle temperature T_B are characteristic constants, which can be evaluated for each substance from PVT data. By inserting d from equation (2) into equation (1), and after introducing the dimensionless reduced quantities

$$\theta = \frac{T}{T_B} \qquad \text{and} \qquad \beta_n = d_0^{(n+1)} B_n \tag{3}$$

relation (1) assumes the following simple form when Z is unity:

$$\sum_{n=0}^{\infty} \beta_n (1 - \theta)^n = 0. \tag{4}$$

Next, by the first, second and further differentiations of series (4) with respect to θ, one gets very useful relations between the virial coefficients at the Boyle temperature (Holleran 1968). For example

$$\beta_1(T_B) = \left(\frac{\partial \beta_0}{\partial \theta} \right)_{T_B} \qquad \beta_2(T_B) = \left(\frac{\partial \beta_1}{\partial \theta} - \frac{1}{2} \frac{\partial^2 \beta_0}{\partial \theta^2} \right)_{T_B}$$

$$\beta_3(T_B) = \left(\frac{\partial \beta_2}{\partial \theta} - \frac{1}{2} \frac{\partial^2 \beta_1}{\partial \theta^2} + \frac{1}{6} \frac{\partial^3 \beta_0}{\partial \theta^3} \right)_{T_B} \tag{5}$$

Now we want to show how Holleran's inter-relations may be applied to our problem of

the summation of the virial expansion. To do this we remark that any reduced virial coefficient β_n at the Boyle temperature can be formally expressed by an appropriate derivate of the second reduced virial coefficient β_0, namely

$$\beta_n(T_{\mathrm{B}}) = \frac{1}{n!}\left(\frac{\partial^n \beta_0}{\partial \theta^n}\right)_{T_{\mathrm{B}}}. \tag{6}$$

There exists a difference between the inter-relations expressed by equations (5) and (6). The second virial coefficient expresses the deviations from the ideal behaviour in terms of two particle interactions only, while the three, and higher body effects are introduced in contributions from the third, and higher virial coefficients, respectively. Expressing any virial coefficient in terms of the appropriate derivate of B_0 thus takes account only of two body forces.

Let us remark that relation (6) can be generalized, to express any virial coefficient β_n at an arbitrary temperature by an appropriate derivate β_0, taken at the Boyle temperature:

$$\beta_n(T) = \sum_{j=0}^{\infty} \frac{1}{n!}\left(\frac{\partial^{(n+j)} \beta_0}{\partial \theta^{(n+j)}}\right)_{T_{\mathrm{B}}} \frac{1}{j!}(\theta - 1)^j. \tag{7}$$

Note additionally that

$$B_0 = -2\pi N\sigma^3 \int_0^{\infty} \mathrm{d}r\, r^2 \sum_{m=1}^{\infty} \frac{1}{m!}\left(\frac{-U(r)}{kT_{\mathrm{B}}\theta}\right)^m \tag{8}$$

where σ and $U(r)$ are the slow-collision molecular diameter and the pair interaction energy, respectively. Next, it is easy to check that

$$\frac{\partial^i}{\partial \theta^i}\left(\frac{-U(r)}{kT_{\mathrm{B}}\theta}\right)^m = \frac{(m+i-1)!}{(m-1)!}(-1)^i\left(\frac{-U(r)}{kT_{\mathrm{B}}}\right)^m \theta^{-(i+m)}. \tag{9}$$

Considering equations (7), (8) and (9), we get

$$\beta_n(T) = \sum_{j=0}^{\infty} \frac{(\theta-1)^j}{j!n!}\, \mathrm{d}_0\left\{\frac{\partial^{(n+j)}}{\partial \theta^{(n+j)}}(-2\pi N\sigma^3)\int_0^{\infty} \mathrm{d}r\, r^2 \sum_{m=1}^{\infty} \frac{1}{m!}\left(\frac{-U(r)}{kT_{\mathrm{B}}\theta}\right)^m\right\}_{T_{\mathrm{B}}} \tag{10}$$

and thence

$$\beta_n(T) = -2\pi N\sigma^3 \mathrm{d}_0 \int_0^{\infty} \mathrm{d}r\, r^2 \sum_{j=0}^{\infty} \sum_{m=1}^{\infty} \frac{(m+n+j-1)!}{n!j!m!(m-1)!}(1-\theta)^j(-1)^n\left(\frac{-U(r)}{kT_{\mathrm{B}}}\right)^m. \tag{11}$$

The compressibility factor is thus given by

$$Z = 1 - 2\pi N\sigma^3 d \int_0^{\infty} \mathrm{d}r\, r^2 \sum_{n=0}^{\infty} \sum_{j=0}^{\infty} \sum_{m=1}^{\infty} \frac{(m+n+j-1)!}{n!j!m!(m-1)!}(1-\theta)^j\left(\frac{-d}{d_0}\right)^n\left(\frac{-U(r)}{kT_{\mathrm{B}}}\right)^m. \tag{12}$$

Note in addition that

$$(j+n+m-1)! = \Gamma(j+n+m) = \int_0^{\infty} \mathrm{d}t\, \mathrm{e}^{-t}t^{(j+m+n-1)}. \tag{13}$$

Thus

$$
Z = 1 - 2\pi N\sigma^3 d \int_0^\infty \mathrm{d}r\, r^2 \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-t} \sum_{n=0}^\infty \frac{1}{n!} \left(\frac{-td}{d_0}\right)^n \sum_{j=0}^\infty \frac{1}{j!} \{t(1-\theta)\}^j
$$
$$
\times \sum_{m=1}^\infty \frac{1}{m!(m-1)!} \left(\frac{-U(r)}{kT_B}\right)^m t^{(m-1)}. \tag{14}
$$

After summation with respect to n and j, we get

$$
Z = 1 - 2\pi N\sigma^3 d \int_0^\infty \mathrm{d}r\, r^2 \sum_{m=1}^\infty \frac{1}{m!(m-1)!} \left(\frac{-U(r)}{kT_B}\right)^m \int_0^\infty \mathrm{d}t \exp\left\{-t\left(\frac{d}{d_0}+\theta\right)\right\} t^{(m-1)}. \tag{15}
$$

Integration by parts yields

$$
\int_0^\infty \exp\left\{-t\left(\frac{d}{d_0}+\theta\right)\right\} t^{(m-1)}\, \mathrm{d}t = (m-1)! \left(\frac{1}{(d/d_0)+\theta}\right)^m. \tag{16}
$$

From equations (15) and (16) it follows that:

$$
Z = 1 - 2\pi N\sigma^3 d_0 \Delta \int_0^\infty \mathrm{d}r\, r^2 \left\{\exp\left(\frac{-U(r)}{kT_B(\Delta+\theta)}\right) - 1\right\} \tag{17}
$$

where Δ, and θ are the so called 'reduced' density and temperature, respectively.

3. Numerical results and discussion

Consider now equation (17). It has been shown by Holleran that both the value $\frac{2}{3}\pi N\sigma^3 d_0$, and U_0/kT_B are the same for all gases interacting via the same potential function U. The Lennard–Jones (12–6) potential has been one of the most widely used, and thoroughly studied, potentials, and it is well known that for it $U_0 kT_B = 3418$, according to Holleran, $\frac{2}{3}\pi N\sigma^3 d_0 = 2397$. The dependence of $\frac{2}{3}\pi N\sigma^3 d_0$ on the type of potential arises from the fact that it is calculated from another of Holleran's relations, namely that

$$
d_0 = \left(\frac{B_0}{(\theta-1)B_1}\right)_{TB}.
$$

As for B_0 and B_1—theoretical expressions were taken by Holleran, which depend of course on the potential assumed. Thus, equation (17) is an equation of state, depending upon two reduced variables Δ and θ.

From the form of equation (17) it follows that there should only be a negligible difference between equation (17) and the truncated series when considering small densities. Therefore, it is of no particular interest to investigate the agreement with experimental data in the region of small densities. On the other hand, one of the most important, and still not completely solved problems of statistical mechanics is the theory of condensed phases, and first order phase transitions.

It is now known that in order to describe a phase transition, it is necessary to take into account the intermolecular interactions of infinite range in some way. This may be

accomplished either by considering directly the limit of infinite-range original inter-
molecular two body potentials (Uhlenbeck and Hemmer 1965, Kac *et al*, 1964, Emch
1967 and Van Kampen 1970), or by arriving at the infinite-range effective intermolecular
force field by the summations of some infinite subsets of terms, describing some formal
expansions of the properties of the system under consideration (Van Leeuven *et al*, 1959,
Morita 1969, Percus and Yevick 1958 and Fuliński 1968, 1970a, 1970b).

The method presented here follows the second idea, and should therefore predict
phase transitions. To prove this, numerical calculations of Z have been performed by
the author for a wide range of densities and temperatures, including critical conditions
for particles interacting via a Lennard–Jones (12–6) potential. In addition appropriate
calculations have been performed by using the truncated series (after the second term)
for the same range of densities and temperatures. The results are presented and com-
pared on figure 1. The calculations have been performed for four reduced temperatures :
$\theta = 0.1$, $\theta = 0.2$, $\theta = 0.3$ and $\theta = 0.4$, respectively. The full curves denote the data
obtained from equation (17), whereas the broken curves denote the data obtained from
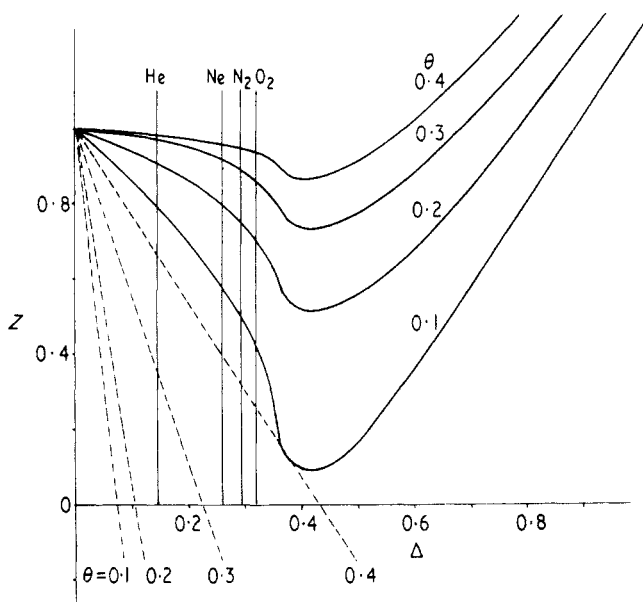the truncated series.

Figure 1. The compressibility factor Z as a function of the reduced density Δ for four
reduced temperatures θ. Full curves denote the data obtained from equation (17), and
broken curves denote the data obtained from the truncated series. The four vertical lines
marked with He, Ne, N_2, and O_2 denote the positions of the experimental critical reduced
densities for these substances.

Considering experimental data for spherical nonpolar molecules, and assuming them
to interact via a Lennard–Jones (12–6) potential, one gets the following approximate
relations that $U_0/k = 0.770T_c$, and $U_0/k = 0.292T_B$ (Hirschfelder *et al* 1954). From this
it follows that the reduced critical temperature θ_c should be equal to 0.4.

The compressibility factor treated as a function of two reduced variables T/T_c,
and p/p_c has been investigated thoroughly by Hougen and Watson (1946). They have

prepared charts of the compressibility factor in a wide region including critical conditions. Their charts were prepared by averaging data for such gases as H_2, N_2, CO_2, CH_4, which on the other hand obey the Holleran's law (except for H_2).

It may be observed that the author's plots based on equation (17), are very similar to those experimental plots prepared by Hougen and Watson, in the whole range of densities and temperatures under investigation.

Note that Z_{min} should be reached for the critical temperature and at a density being very near, though a little higher, than the critical density Δ_c. The author has evaluated the critical reduced densities Δ_c for four substances: He, Ne, N_2 and O_2, to investigate the agreement with the minimum point Δ_{min} for $\theta_c = 0.4$. The four vertical lines marked He, Ne, N_2 and O_2 in figure 1 denote the positions of the experimental Δ_c for these four substances. It is seen from figure 1 that there is very good agreement for Ne, N_2 and O_2, but worse for He. The deviation for helium is probably due to quantum effects.

However, there exist some serious discrepancies too, between our theoretical and experimental results, when considering the 'critical compressibility factor', defined as $p_c V_c / R T_c$. It is well known that its value is the same for all simple gases, and is equal to 0.3, instead of 0.9, as is found by us. In the author's opinion it is probably due to deviations of the potentials which really exist in simple gases, from the Lennard–Jones (12–6) potential. It may be that neglecting of the three and higher body forces plays a remarkable role here. Their contribution to the thermodynamic properties of systems should increase as the density increases.

Next, the author has plotted the reduced density Δ as a function of the reduced temperature θ under the condition that Z is unity. The results are presented in figure 2. It follows from figure 2 that the agreement is in excellent accordance with Holleran's unit compressibility law.
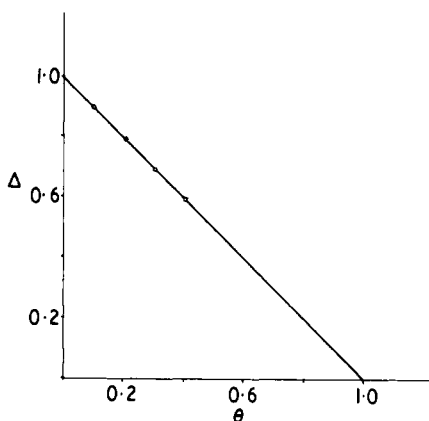

Figure 2. The reduced density Δ, plotted from equation (17), as a function of the reduced temperature θ, under the condition that Z is unity.

The integration in equation (17) can be performed analytically for some interaction potentials; for example, the rigid-sphere, the square-well, the Sutherland and the Lennard–Jones (12–6) potentials. This is an additional advantage of the method presented in this paper.

Acknowledgments

References

Emch G G 1967 *J. math. Phys.* **8** 13–9
Fuliński A 1968 *Acta Phys. Pol.* **33** 281–91, **34** 91–100
—— 1970a *Phys. Lett.* **31A** 176–7
—— 1970b *Acta Phys. Pol.* **37** 177–84, 185–93
Hirschfelder J O, Curtis C F and Bird R B 1954 *Molecular Theory of Gases and Liquids* (New York: Wiley)
Holleran E M 1967 *J. chem. Phys.* **47** 5318–23
—— 1968 **49** 39–43
Hougen O A and Watson K M 1946 *Chemical Processes Principle Charts* (Madison, Wisconsin: Democrat Printing Co)
Kac M, Uhlenbeck G E and Hemmer P C 1964 *J. math. Phys.* **5** 60 see also **4** 216–29
Van Kampen N G 1970 *Physica* **48** 313
Van Leeuven J M, Groeneveld J and De Boer J 1959 *Physica* **25** 792
Morita T 1969 *Prog. theor. Phys.* **41** 339
Percus J K and Yevick G J 1958 *Phys. Rev.* **110** 1
Stell G 1963 *Physica* **19** 517
Uhlenbeck G E and Hemmer P C 1965 *Statistical Mechanics of Equilibrium and Nonequilibrium* (Amsterdam: North-Holland)