

### The Equation of State of a Fluid

Equation d'état d'un fluide

J. L. LEBOWITZ,<sup>1</sup> H. L. FRISCH<sup>2</sup> and H. REISS<sup>2</sup>,  
U.S.A.

*SOMMAIRE.* Le travail nécessaire pour former une lacune dans un fluide est en rapport étroit avec son équation d'état, et avec la probabilité de trouver une telle lacune en équilibre. En cas d'un fluide consistant des molécules à noyau non pénétrable cette possibilité existe pour des lacunes petites, mais (en général) pour les lacunes plus grandes et travail est donné au terme de pression-volume. Ce dernier et certaines considérations thermodynamiques donnent une formule approximative d'interpolation pour les lacunes de grandeur quelconque. Pour un fluide à sphère dure (aucune force d'attraction) le résultat est un rendement d'une simple équation analytique d'état a bien d'accord avec l'équation obtenue empiriquement par computation à machine et l'expansion viriale [1]. Quand les forces d'attraction ne sont pas négligées, la théorie préalable donne les expressions de la tension superficielle, le coefficient de solubilité - loi de Henry, et l'équation d'état «haute température». Les résultats correspondent assez bien avec les mesures expérimentales des fluides simples. Il est très intéressant d'étendre ces relations aux fluides à températures très basses où les fluctuations quantiques sont décisives.

Même que quelques-unes des relations dérivées préalablement ne nécessitent que des modifications peu considérables, d'autres, i.e. la relation entre travail et probabilité en exigent des changements drastiques.

#### INTRODUCTION

The pressure of a fluid whose molecules interact with pairwise central forces derivable from a potential  $\varphi(r)$ , is given by [2]

$$p = \rho kT - \frac{2\pi}{3} \rho^2 \int_0^\infty \frac{d\varphi}{dr} g(r) r^3 dr \tag{1.1}$$

Here  $\rho$  is the density (number of molecules per unit volume),  $k$  is Boltzmann's constant, and  $g(r)$  is the pair correlation function. For a very large system consisting of  $N$  molecules in a container of volume  $V$ ,  $g(r)$  has the form

$$g(r_{12}) = \frac{V^2 \int_V \dots \int_V \exp \left[ -\frac{1}{2kT} \sum_{i,j=1}^N \varphi(r_{ij}) \right] \vec{dr}_3 \dots \vec{dr}_N}{\int \int \exp \left[ -\frac{1}{2kT} \sum_{i,j=1}^N \varphi(r_{ij}) \right] \vec{dr}_1 \dots \vec{dr}_N} \tag{1.2}$$

Since the explicit evolution of  $g(r)$  presents insurmountable difficulties (except for an ideal gas when  $\varphi = 0$ ,  $g(r) = 1$ , and  $p = \rho kT$ ) some approximation methods

<sup>1</sup> Supported by the U.S. Air Force Office of Scientific Research, Stevens Institute of Technology, Hoboken, New Jersey.  
<sup>2</sup> Bell Telephone Laboratories, Murray Hill, New Jersey.



have to be devised for obtaining quantitative results. There are now several such methods but we shall only discuss two of them.

The first method develops  $g(r)$  and thus  $p$  in a power series in the density  $\rho$ . This leads to the well-known virial expansion of Van der Waals [2]

$$p = \rho kT \left[ 1 + \sum_{n=1}^{\infty} B_n \rho^n \right] \quad (1.3)$$

The  $B_n$  are given by the Mayer cluster integrals each  $B_n$  involving an  $n$ -fold integration.

The second method developed by Yvon, Born-Green and Kirkwood [2] utilizes an approximate integral equation for  $g(r)$ . Solution of this equation and substitution in (1.1) yields  $p$ .

Both of these two methods suffer from severe handicaps. The virial expansion, while rigorous, is useful only for (sufficiently) dilute gases. Even then the evaluation of the  $B_n$  is extremely difficult. Only in the case of the hard sphere gas, i. e., where the molecules are treated as rigid spheres, have the first few virial coefficients been computed analytically. The integral equation method suffers from the fact that it is based on the superposition approximation, [i. e., the probability that particles 1, 2, 3 are at positions  $\vec{r}_1, \vec{r}_2, \vec{r}_3$ , is assumed to be a product of the probabilities

that 1 and 2 are at  $\vec{r}_1$  and  $\vec{r}_2$ , 2 and 3 are at  $\vec{r}_2$  and  $\vec{r}_3$  and 1 and 3 are at  $\vec{r}_1$  and  $\vec{r}_3$ ] whose validity or range of validity has not been established. It possesses the further difficulty that the solution of the integral equation can be accomplished only numerically, after first simplifying it, thus introducing new approximations. For this method too the hard sphere gas serves as an appropriate test case.

#### HARD SPHERE GAS

The importance of the hard sphere fluid is not limited entirely to its theoretical usefulness as a model of a many body system. At very high temperatures, when the kinetic energy of a gas molecule is much greater than the minimum value of  $\varphi$ , the hard core is all important in determining the properties of the fluid. Similarly, at very high densities the attractive part of  $\varphi$  may be thought of as a smoothed average potential not greatly affecting the properties of the fluid. Our new method was therefore developed first for this model fluid.

Calling  $a$  the diameter of a hard sphere molecule, the potential  $\varphi(r)$  has the form

$$\varphi(r) = \begin{cases} \infty, & r < a \\ 0, & r > a \end{cases} \quad (2.1)$$

After some manipulation the virial equation, Equation (1.1), becomes

$$\frac{p}{\rho kT} = 1 + \frac{3}{2} \pi \rho a^3 g(a) \quad (2.2)$$

It is evident from the above equation that only  $\rho g(a)$ , the probability density for having two spheres in contact is necessary for finding the equation of state. Our method for finding  $g(a)$  is to introduce first a new function  $p_0(r)$ , the probability of finding a spherical cavity of at least radius  $r$  centered about some specified point in the fluid. A cavity is defined as a region of space devoid of molecules (i. e., their centres). The negative rate of change of  $p_0$ ,  $-\frac{dp_0}{dr} dr$  is clearly the probability of finding a cavity whose radius lies between  $r$  and  $r + dr$ . This proba-



bility is in turn equal to the product of the probability of having a cavity of at least radius  $r$ ,  $p_0(r)$ , and the conditional probability of there being a center of some molecule between  $r$  and  $r + dr$  when there is none inside the sphere of radius  $r$ . We call this conditional probability  $\rho G(r)4\pi r^2 dr$ . Thus

$$-\frac{dp_0}{dr} = p_0(r)4\pi r^2 \rho G(r) \quad (2.3)$$

From the definition of  $G(r)$  it follows that  $G(a) = g(a)$ . We can also show from the general principles of classical statistical mechanics that the probability for the spontaneous occurrence of some specified situation is equal to the negative exponential of the reversible work necessary to create that situation [2]. Thus

$$p_0(r) = e^{-\frac{W(r)}{kT}} \quad (2.4)$$

where  $W(r)$  is the reversible work necessary to create a cavity of size  $r$  in the liquid.

The work  $dW$  necessary to increase the radius of the cavity will in general be given by

$$dW = p dv + \sigma dS = kT \rho G(r) dv \quad (2.5)$$

Here  $dv$  is the change in volume of the cavity ( $4\pi r^2 dr$ ),  $dS$  the change in its surface area ( $8\pi r dr$ ), and  $\sigma$  is the surface tension. Since the surface of the cavity is impenetrable to the molecules it behaves like a rigid wall and  $\sigma$  measures the surface tension of hard sphere molecules against the rigid walls of a spherical cavity of radius  $r$ . Combining (2.3), (2.4) and (2.5) yields

$$G(r) = \frac{p}{\rho kT} + \frac{\sigma}{\rho kT 2r}, \quad r \text{ not too small} \quad (2.6)$$

Thermodynamic considerations on the surface tension of spherical bubbles as well as some detailed investigations on the structure of  $G(r)$  suggest that for not too small  $r$ ,  $\sigma$  should have the form

$$\sigma(r) = \sigma_0 \left( 1 + \frac{2\delta a}{r} \right) \quad (2.7)$$

where  $\sigma_0$  is the surface tension against a flat wall and  $\delta$  is a dimensionless parameter. When this is substituted in (2.6) we find

$$G(r) = \frac{1}{\rho kT} \left[ p + \frac{\sigma_0}{2r} + \frac{\sigma_0 \delta a}{r^2} \right] \quad (2.8)$$

Note that this gives

$$G(\infty) = \frac{p}{\rho kT} = 1 + \frac{3}{2}\pi \rho a^3 G(a) \quad (2.9)$$

This result can also be derived from the following consideration. The normal stress at the surface of a cavity is purely kinetic and is equal to  $kT$  times the density at the surface  $\rho G(r)$  as is seen from Equation (2.5). As the cavity becomes very large its surface approaches that of a plane and the normal stress becomes equal to  $p$ .<sup>3</sup>

<sup>3</sup> It follows from this discussion that the density of an arbitrary fluid near a rigid wall  $\rho_w$  is related to its pressure by  $p = \rho_w kT$ .

Evaluating Equation (2.8) for  $r = a$  we find an expression for  $G(a)$  and hence for the pressure in terms of  $\sigma_0$  and  $\delta$ .

In order to determine these constants we go back to our definition of  $p_0$  as the probability of having no particles inside the cavity. This is clearly equal to the probability of all particles being *outside* the cavity. We therefore have

$$p_0(r) = \frac{\int_{V'} \dots \int_{V'} \exp \left[ -\frac{1}{2kT} \sum_{i=1}^N \varphi(r_{ij}) \right] d\vec{r}_1 \dots d\vec{r}_N}{\int_V \dots \int_V \exp \left[ -\frac{1}{2kT} \sum_{i=1}^N \varphi(r_{ij}) \right] d\vec{r}_1 \dots d\vec{r}_N} \quad (2.10)$$

where  $V$  is the volume of the box containing the system and  $V'$  is the volume of the box exclusive of the sphere of radius  $r$  (about some specified point  $\vec{R}$ ). By introducing the Heaviside unit function  $\varepsilon$

$$\varepsilon(\vec{r}_i) = \begin{cases} 1, & |\vec{r}_i - \vec{R}| > r \\ 0, & |\vec{r}_i - \vec{R}| < r \end{cases} \quad (2.11)$$

Equation (2.10) can be rewritten as

$$p_0(r) = \frac{\int_V \dots \int_V \prod_{i=1}^N \left( (1 - \varepsilon(\vec{r}_i)) e^{-\frac{1}{2kT} \sum \varphi(r_{ij})} \right) d\vec{r}_1 \dots d\vec{r}_N}{\int_V \dots \int_V e^{-\frac{1}{2kT} \sum \varphi(r_{ij})} d\vec{r}_1 \dots d\vec{r}_N} \quad (2.12)$$

$$= 1 - \sum_{n=1}^N (-1)^n F_n$$

where  $F_n$  is the *average* number of  $n$ -tuplets in the spherical region of radius  $r$ . Thus

$$F_1 = \rho \frac{4}{3} \pi r^3 \quad (2.13)$$

$$F_2 = \frac{1}{2} \int \int_{\left[ \begin{array}{c} \text{sphere of} \\ \text{radius } r \end{array} \right]} \rho^2 g(r) d\vec{r}_1 d\vec{r}_2$$

It is now seen that for  $r < \frac{a}{2}$ , when no more than one particle can be accommodated inside the cavity we must have  $F_2 = F_3 = \dots = F_n = 0$ , and thus



$$p_0(r) = 1 - \rho \frac{4}{3} \pi r^3, r \leq \frac{a}{2} \quad (2.14)$$

$$G(r) = \frac{1}{1 - \frac{4}{3} \pi r^3 \rho}, r \leq \frac{a}{2}$$

It can further be shown that at  $r = \frac{a}{2}$ ,  $G$  and its derivative are both continuous at  $r = \frac{a}{2}$ . We now assume, and this is the crux of our approximation, that (2.6) holds down to  $r = \frac{a}{2}$ . When the values of  $G\left(\frac{a}{2}\right)$  and  $\left(\frac{dG}{dr}\right)_{r=\frac{a}{2}}$  derived from (19) are now substituted into (2.6) we get two equations determining  $\sigma_0$  and  $\delta$  and through them the equation of state (c.f. (2.8)).

This approximate equation of state is in the form of (2.2) with

$$g(a) = \frac{1}{4}y + \frac{3}{4}y^2 + \frac{\pi a^3 \rho}{8y^3}, \quad (2.15)$$

$$y = 1 - \frac{\pi a^3 \rho}{6}$$

Expanded in powers of the density, (2.15) gives exactly the first three virial coefficients with an error of only 2% in the fourth and a 5% error in the fifth virial coefficient. The agreement of (2.15), over all densities in the fluid range, with the machine computations of Alder and Wainwright [3], shown in Fig. 1, is also satisfactory.

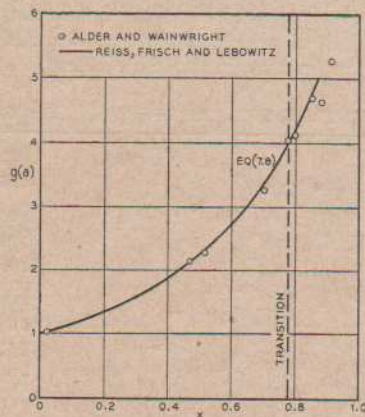


Fig. 1. Approximate equation of state.

Before we consider the question of whether these results can be extended to apply also to the quantum hard sphere fluid we shall apply the foregoing theory to calculate approximately certain properties of real fluids.

#### APPLICATIONS TO REAL FLUIDS

The same argument given in the preceding section can be applied to the calculation of the reversible work necessary for producing a cavity in a real fluid pos-



sessing a hard core (*i. e.*, one possessing a potential consisting of a hard sphere cutoff, at  $r = a$  and a smooth part  $\varphi_2$ ). Again we can define a quantity  $G(r)$ ,  $r$  being the radius of the cavity, which has also here the significance that  $\rho G(r)$  measures the average density of molecules just outside the cavity. It can be shown that both  $G$  and  $G'(r)$  are continuous at  $a/2$  (continuity conditions) and  $G$  has the form given by (2.14) for  $r < a/2$ .

Since (2.6) holds again in sufficient approximation and  $\sigma$  in (2.6) has a curvature dependence,  $G$  will be a quadratic form in  $1/r$ . This implies, through (2.3) and (2.4), that the work,  $W$ , required to form the cavity is a cubic polynomial in  $r$ . The four coefficients in this cubic are determined by the continuity conditions, the known value of  $W$  at  $a/2$  and a known relation between the cubic coefficient and the pressure-volume work done on the surrounding real fluid. Since the work required to form a cavity is the same as that of introducing a hard sphere into the real fluid we know to the indicated approximation the chemical potential  $\mu_h$  of a dilute hard sphere solute. By using a coupling parameter  $\xi$  which charges the nonhard sphere part of the intermolecular potential we can write the chemical potential of a real solute  $\mu$  as the sum

$$\mu = \mu_h + \int_0^1 d\xi \int_0^\infty 4\pi r^2 \varphi_2(r) g(r, \xi) dr \quad (3.1)$$

where  $g$  is the radial distribution function of the solute in the fluid for the indicated value of the coupling parameter  $\xi$ .

By using thermodynamic identities we can now calculate using (2.16) such entities as:

- (1) the vapor pressure of the pure fluid when the density of the liquid phase at a given temperature is known in addition to  $a$ ,
- (2) the heat of vaporization (using also the experimental value of the coefficient of thermal expansion),
- (3) Henry's Law constants.

Furthermore the boundary tension of a fluid against a rigid wall can be computed (as well as its dependence on curvature) and the values thus derived compared with the surface tension which it should approximate. Comparison of these quantities with experiment for Argon appears in the table below:

TABLE 1. PHYSICAL PROPERTIES OF ARGON

Computed Property	Measured Property
Rigid Wall boundary tension 85.1° K. 16.4 dynes/cm	Surface Tension against vapor 85.1° K. 13.2 dynes/cm
Heat of Vaporization at 87.2° K. 1510 calories/mole	Heat of Vaporization at 87.2° K. 1500 calories/mole
Henry's Law Constant of He in Argon 86.89° K. $9.35 \times 10^5$ cm Hg	Henry's Law Constant of He in Argon 86.89° K. $3.31 \times 10^5$ cm Hg

## REFERENCES

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