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Gibbs adsorption and the compressibility equation

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A new approach for deriving the equation of state is developed. It is shown that the integral in the compressibility equation is identical to the isotherm for Gibbs adsorption in radial coordinates. The Henry, Langmuir, and Frumkin adsorption isotherms are converted into equations of state. It is shown that using Henry's law gives an expression for the second virial coefficient that is identical to the result from statistical mechanics. Using the Langmuir isotherm leads to a new analytic expression for the hard-sphere equation of state which can be explicit in either pressure or density. The Frumkin isotherm results in a new equation of state for the square-well potential fluid. Conversely, new adsorption isotherms can be derived from equations of state using the compressibility equation. It is shown that the van der Waals equation gives an adsorption isotherm equation that describes both polymolecular adsorption and the unusual adsorption behavior observed for supercritical fluids. © 1995 American Institute of Physics.

INTRODUCTION

Two-dimensional equations of state have been used for some time to calculate monolayer adsorption isotherms through the Gibbs integral. The reverse process of using an isotherm to derive the corresponding two-dimensional equation of state also is well known.

In this paper adsorption isotherms are related to the three-dimensional equation of state using the compressibility equation. In this equation the integrand can be represented by the difference between local density and bulk density, the integral is the Gibbs adsorption in spherical coordinates, i.e., the "adsorption" of molecules on a central molecule. This approach is similar to ideas used in development scaled particle theory (SPT), where a spherical "hole" or cavity is considered to be in equilibrium with surrounding fluid and the surface tension at the boundary of the "fluid cavity" is the key parameter.

The purpose of this paper is to show that the concepts used in SPT can be applied more rigorously and with fewer assumptions using the compressibility equation. It is hoped that this new approach might be helpful in extending the techniques of SPT to real fluids.

COMPRESSIBILITY EQUATION AND GIBBS ADSORPTION

The compressibility equation for one component fluid with a spherical symmetry of intermolecular interactions can be written in the form¹

$$kT \left(\frac{\partial \rho}{\partial P} \right)_{T,N} = 1 + 4\pi\rho \int_0^\infty [g(r) - 1] r^2 dr, \quad (1)$$

where ρ is the density, P is the pressure, $g(r)$ is the radial distribution function, N is the number of molecules in a system, T is the absolute temperature, and k is the Boltzmann constant.

Equation (1) can be rewritten as

$$\left[\frac{\partial(\rho kT - P)}{\partial P} \right]_{T,N} = \int_0^\infty [\rho(r) - \rho(\infty)] 4\pi r^2 dr, \quad (2)$$

where

$$\rho(r) = \rho g(r) \quad (3)$$

and

$$\rho(\infty) = \rho. \quad (4)$$

The integral in the right-hand side of Eq. (2) is the same as the classical definition for Gibbs adsorption, $\Gamma(P)$, for a system with spherical symmetry, i.e.,

$$\Gamma(P) = \int_0^\infty [\rho(r) - \rho(\infty)] 4\pi r^2 dr. \quad (5)$$

The value of Γ determined from Eq. (5) can be interpreted as the excess adsorption of fluid around one molecule of the same fluid.

This analogy to adsorption behavior can be used to derive equations of state from adsorption isotherms. From Eqs. (2) and (5) it follows that

$$\left[\frac{\partial(\rho kT - P)}{\partial P} \right]_{T,N} = \Gamma(P). \quad (6)$$

LOW PRESSURE LIMIT

In the low pressure limit, the dependence of Γ on P is given by Henry's law,

$$\Gamma = HP, \quad (7)$$

where H is the Henry's law coefficient.

Substituting Eq. (7) into Eq. (6) gives

$$\rho kT - P = \int_0^P HP dP = HP^2/2. \quad (8)$$

From Eq. (8) it follows that

$$P = 2\rho kT/[1 + (1 + 2\rho kTH)^{1/2}]. \quad (9)$$

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Expansion of the right side of Eq. (9) in a series in powers of ρ gives

$$P/\rho kT = 1 - kTH\rho/2 + (kTH\rho)^2/2 - 5(kTH\rho)^3/8 + \dots \quad (10)$$

Thus the second virial coefficient, B_2 , is

$$B_2 = -kTH/2. \quad (11)$$

From Eqs. (3)–(5), (7), (11) we obtain

$$B_2 = -(kT\rho/2P) \int_0^\infty [g(r) - 1] dr. \quad (12)$$

It follows from the ideal gas law and from Eq. (8) that

$$\lim_{P \rightarrow 0} (kT\rho/P) = 1. \quad (13)$$

Therefore, from Eq. (12) we get

$$B_2 = -(1/2) \int_0^\infty [g(r) - 1] dr. \quad (14)$$

Equation (14) is the well known equation for the second virial coefficient.¹ This implies that using of Henry's law for the integral in Eq. (2) gives the correct low pressure limit for B_2 .

LANGMUIR APPROXIMATION

Langmuir² derived an expression for the adsorption isotherm assuming that there no attractive interactions between adsorbate molecules. This is equivalent to assuming that the adsorbate molecules are hard spheres. The Langmuir isotherm is written as

$$\Gamma = HP/(1 + BP), \quad (15)$$

where B is a coefficient which is related to the capacity of adsorption [the parameter B used in Eq. (15) is not related to the second virial coefficient B_2]. This expression is widely used to model adsorption of fluids on solid or liquid surfaces³ when there are deviations from linear behavior.

Substituting Eq. (15) into Eq. (6) one gets

$$\rho kT - P = (H/B)P - (H/B^2)\ln(1 + BP). \quad (16)$$

An expansion of right side of Eq. (16) in a series results in

$$\rho kT = P + (H/2)P^2 - (HB/3)P^3 + (HB^2/4)P^4 - (HB^3/5)P^5 + (HB^4/6)P^6 - \dots \quad (17)$$

Inverting⁴ the expansion in Eq. (17) we get

$$\begin{aligned} P/\rho kT = & 1 - (H/2)kT\rho + (H^2/2 + HB/3)(kT\rho)^2 \\ & - (5H^3/8 + 5H^2B/6 + HB^2/4)(kT\rho)^3 + (7H^4/8 \\ & + 7H^3B/4 + 13H^2B^2/12 + HB^3/5)(kT\rho)^4 \\ & - (21H^5/16 + 7H^4B/2 + 119H^3B^2/36 \\ & + 77H^2B^3/60 + HB^4/6)(kT\rho)^5 + \dots \end{aligned} \quad (18)$$

A similar transformation was used in the Mayer cluster expansion.¹

If we define

$$b_0 \equiv B_2 = -(H/2)kT \quad (19)$$

then the third and higher virial coefficients are

$$B_3 = (2 + 4B/3H)b_0^2, \quad (20)$$

$$B_4 = (5 + 20B/3H + 2B^2/H^2)b_0^3, \quad (21)$$

$$B_5 = (14 + 28B/H + 52B^2/H^2 + 16B^3/5H^3)b_0^4, \quad (22)$$

$$\begin{aligned} B_6 = & (42 + 112B/H + 952B^2/9H^2 + 616B^3/15H^3 \\ & + 16B^4/3H^4)b_0^5. \end{aligned} \quad (23)$$

COMPARISON WITH THE HARD-SPHERE EQUATION OF STATE

For the hard-sphere fluid

$$\lim_{P \rightarrow \infty} \left(\frac{\partial \rho}{\partial P} \right)_{T,N} = 0. \quad (24)$$

Therefore, it follows from Eqs. (1)–(6) that

$$\Gamma(P = \infty) = -1. \quad (25)$$

Comparing this with Eq. (15) we obtain

$$B/H = -1. \quad (26)$$

Substituting $B/H = -1$ into Eq. (16) one obtains, after transformations

$$P/\rho kT = [\exp(B\rho kT) - 1]/B\rho kT. \quad (27)$$

The expansion of the right side of Eq. (27) in a series in ρ gives

$$\begin{aligned} P/\rho kT = & 1 + b_0\rho + (2/3)b_0^2\rho^2 + (1/3)b_0^3\rho^3 \\ & + (2/15)b_0^4\rho^4 + (2/45)b_0^5\rho^5 + \dots, \end{aligned} \quad (28)$$

where

$$b_0 = BkT/2. \quad (29)$$

With Eq. (29), Eq. (27) can be written in the form

$$Z = P/\rho kT = [\exp(2b_0\rho) - 1]/(2b_0\rho). \quad (30)$$

The most commonly used expressions for the reduced density, y , and the diameter of spherical molecule σ , for hard-sphere fluid are

$$y = (\pi/6)\rho\sigma^3, \quad (31)$$

$$b_0 = B_2 = (2/3)\pi\sigma^3. \quad (32)$$

Using these, we get from Eqs. (30)–(32) that

$$b_0\rho = 4y \quad (33)$$

and therefore it follows from Eq. (30)

$$Z = [\exp(8y) - 1]/(8y). \quad (34)$$

The expansion of this equation in powers of y is

$$\begin{aligned} Z = & 1 + 4y + (32/3)y^2 + (64/3)y^3 + (512/15)y^4 \\ & + (2048/45)y^5 + (16384/315)y^6 + \dots \end{aligned} \quad (35)$$

Figure 1 shows the dependence of Z on y for Eq. (34), for the Percus–Yevick pressure equation (PYP), the Percus–Yevick compressibility equation (PYC) (which is equivalent to the result from SPT), the Carnahan–Starling equation

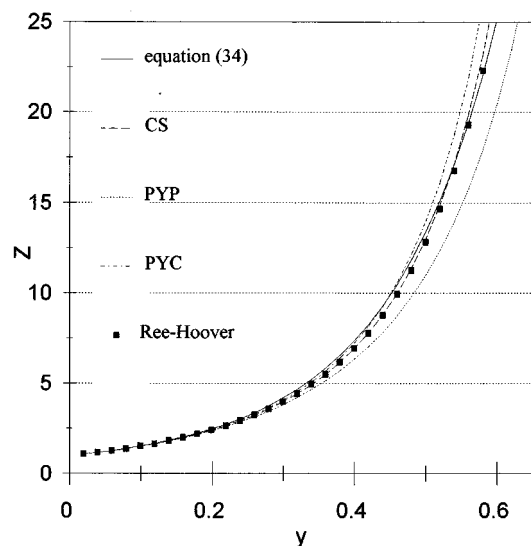


FIG. 1. Dependence of Z on y for Eq. (34), PYP, PYC, and CS models, and for Ree-Hoover approximant.

(CS), and the Ree-Hoover equation.⁵ It can be seen from Fig. 1 that Eq. (34) gives a very good approximation for the hard-sphere equation of state.

Equation (26) indicates that the Langmuir adsorption isotherm is negative, at least for the hard-sphere system. This can be understood by considering adsorption of a fluid in the pore that is too small to be accessible to adsorbate molecules. Gibbs adsorption in the pore is $\Gamma = (\rho_i - \rho_f)V_i$ where ρ_i is the adsorbate density in the pore, ρ_f is the density of fluid, V_i is the volume of pore. For an inaccessible pore $\rho_i = 0$ and therefore $\Gamma < 0$. For $\rho_f = 1$ we have $\Gamma/V_i = -1$. For the case of Eq. (5), we have the space occupied by one hard-sphere molecule. This space is inaccessible to all other molecules and therefore $\Gamma < 0$.

EQUATION OF STATE FOR SQUARE-WELL POTENTIAL

For square-well potential the second virial coefficient B_2 is

$$B_2 = 2\pi\sigma^3\psi/3, \quad (36)$$

where

$$\psi = 1 - (R^3 - 1)[\exp(\epsilon/kT) - 1]. \quad (37)$$

In Eq. (37), R is the range of the square-well attraction, ϵ is the depth of square-well potential.

The Langmuir model assumes hard-sphere interactions between the adsorbate molecules. In order to treat an attractive potential we consider the Frumkin isotherm⁶ for a one-component system. The Frumkin isotherm is a generalization of Langmuir model that takes into account the attractive forces between adsorbate molecules. This isotherm is

$$\Gamma = HPq/(1 + BPq), \quad (38)$$

where

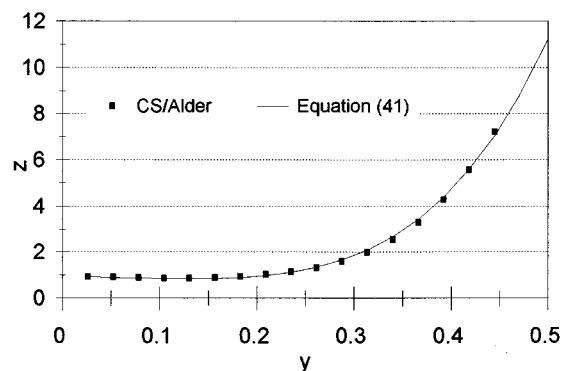


FIG. 2. Comparison of compressibility factor versus reduced density. Calculations are for Eq. (41) and the Carnahan-Starling equation with Alder's fourth-order perturbation expansion.

$$q = \exp(\alpha\Gamma) \quad (39)$$

and α is a temperature-dependent coefficient.

Solving the set of Eqs. (6) and (38) with respect to P and using Eqs. (24)–(26) we get after transformations and expansion

$$\begin{aligned} P/\rho kT = & 1 - (1/2)HkT\rho + (1/6 - \alpha/3)(HkT\rho)^2 - (3\alpha^2/8 \\ & - \alpha/12 + 1/24)(HkT\rho)^3 - (8\alpha^3/15 + 17\alpha^2/120 \\ & + \alpha/30 - 1/120)(HkT\rho)^4 + \dots \end{aligned} \quad (40)$$

Taking into account Eqs. (31), (36), and (37) we get from Eq. (40)

$$\begin{aligned} P/\rho kT = & 1 + 4\psi y + (1/6 - \alpha/3)64\psi^2 y^2 \\ & + (3\alpha^2/8 - \alpha/12 + 1/24)512\psi^3 y^3 - (8\alpha^3/15 \\ & + 17\alpha^2/120 + \alpha/30 - 1/120)4096\psi^4 y^4 + \dots \end{aligned} \quad (41)$$

Equation (41) represents a generalization of Eq. (35) for molecules with an attractive potential. If $\psi = 1$ and $\alpha = 0$ then Eq. (41) reduces to Eq. (35). Here, the coefficient α is treated a temperature-dependent, adjustable parameter.

Figure 2 presents the dependence of Z on y for Eq. (41) with $\alpha = -1.165$. These calculations are compared to those using the Carnahan-Starling equation with Alder's fourth order perturbation expression⁷ for $kT/\epsilon = 2$. It can be seen from Figure 2 that equation (41) is a good approximation over the range of y from 0 to about 0.45.

It is common to write the compressibility as a sum of repulsive and attractive contributions, i.e.,

$$Z = Z_{\text{att}} + Z_{\text{rep}}, \quad (42)$$

where Z is a total compressibility factor, Z_{att} is a contribution of attractive forces, Z_{rep} is a contribution of repulsive forces. Since Z is given by Eq. (41) and value of Z_{rep} is given by Eq. (35), Z_{att} can be calculated by the difference between Eqs. (41) and (35)

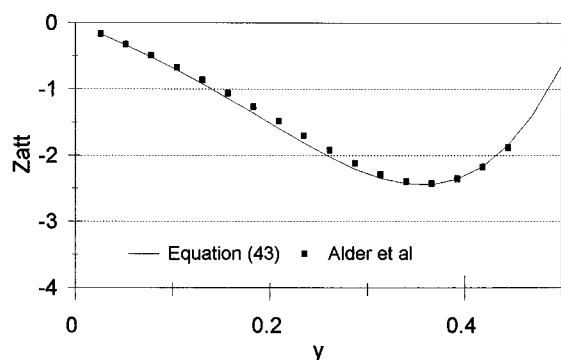


FIG. 3. Contribution of attractive forces to the compressibility factor for $kT/E=2$ and $\alpha=-1.165$.

$$Z_{\text{att}} = 4(\psi - 1)y + 32[(1 - 2\alpha)\psi^2 - 1]y^2/3 + 64[(1/3 - 2\alpha/3 + 3\alpha^2)\psi^3 - 1]y^3/3 + 512[(1 - 4\alpha - 17\alpha^2 - 64\alpha^3)\psi^4 - 1]y^4/15 + \dots \quad (43)$$

Figure 3 presents dependence of Z_{att} on y for Eq. (43). Also shown in Fig. 3 are results from Alder *et al.*⁷ It can be seen that Eq. (43) gives a good fit to the data obtained by computer simulations⁷ with only one adjustable parameter, α .

ADSORPTION ISOTHERMS IN TERMS OF DENSITY

The function Γ in Eqs. (5) and (6) can be considered a function of ρ instead of P and the integral in Eq. (5) can be represented as a sum of two terms

$$\Gamma(\rho) = \Gamma_1(\rho) + \Gamma_2(\rho) \quad (44)$$

so that

$$\Gamma_1(\rho) = \int_0^\sigma [\rho(r) - \rho(\infty)] 4\pi r^2 dr \quad (45)$$

and

$$\Gamma_2(\rho) = \int_\sigma^\infty [\rho(r) - \rho(\infty)] 4\pi r^2 dr. \quad (46)$$

If $\rho(r)=0$ for $r < \sigma$ then

$$\Gamma_1(\rho) = -(4/3)\pi\sigma^3\rho(\infty) = -(4/3)\pi\sigma^3\rho \quad (47)$$

and

$$\Gamma(\rho) = -(4/3)\pi\sigma^3\rho + \Gamma_2(\rho). \quad (48)$$

If we assume that

$$\Gamma_2(\rho) = \lambda\rho^2 \quad (49)$$

and substitute Eq. (48) into Eq. (6) then after integrating we get for $\lambda = (2\pi\sigma^3/3)^2$ that $Z = 1/(1 - 4y)$ which is exactly van der Waals equation for a hard-sphere fluid.

Simple models of adsorption behavior consider only adsorbent and adsorbate interactions. In Eq. (5) the role of adsorbent may be ascribed to one molecule of the fluid, and the adsorbate includes all the other molecules. Therefore, the value of $\Gamma_2(\rho)$ may be interpreted as a conventional adsorp-

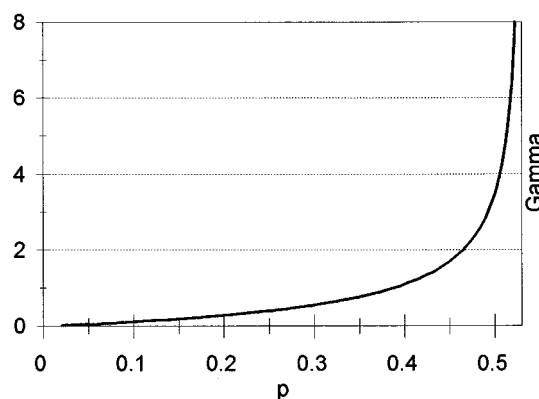


FIG. 4. Adsorption isotherm from van der Waals equation for $T=0.8 T^*$.

tion isotherm and $\Gamma_1(\rho) = -(4/3)\pi\sigma^3\rho$ is the “adsorption” in the inaccessible space occupied by the molecule/adsorbent.

For the Ono-Kondo model of monolayer adsorption,⁸ $\Gamma_2(\rho)$ may be represented as

$$\Gamma_2(\rho) = z_M \rho(1 - \rho)[1 - \exp(-\epsilon/kT)]/[\rho + (1 - \rho) \times \exp(-\epsilon/kT)], \quad (50)$$

where z_M is the monolayer capacity (in the units of volume). Substituting Eq. (50) into Eq. (6), integrating and calculating the compressibility factor gives a second virial coefficient that is the exact result [Eq. (36)] for the square-well fluid if

$$z_M = (4/3)\pi\sigma^3(R^3 - 1). \quad (51)$$

This value is equivalent to the maximum coordination number (in the units of volume) for the square-well fluid.⁹

ISOTHERMS OF GIBBS ADSORPTION FROM COMPRESSIBILITY EQUATION

We have shown that the equation of state can be derived from Eq. (6) if the adsorption isotherm is known. The reverse process also is possible giving the adsorption isotherm from an equation of state. To illustrate this we consider the classical van der Waals equation of state and calculate the value of $\Gamma = kT(\partial\rho/\partial P)_{T,N} - 1$. After straightforward manipulations we get

$$\Gamma = [1 - 8T^*/3(1 - \rho^*/3)^2 + 6\rho^*]/[8T^*/3(1 - \rho^*/3)^2 - 6\rho^*], \quad (52)$$

where ρ^* and T^* are the reduced density and temperature of van der Waals equation of state

$$(P^* + 3\rho^{*2})(1/\rho^* - 1/3) = 8T^*/3. \quad (53)$$

The values $P^* = 1$, $\rho^* = 1$, and $T^* = 1$ correspond to the critical values of pressure P_c , density ρ_c and temperature T_c .

Figure 4 illustrates the dependence of Γ on P for $T^* = 0.8$. Although this adsorption isotherm is for adsorption of fluid around one molecule of the same fluid, it can be seen that the calculated isotherm corresponds to the typical behavior of polymolecular adsorption on a weakly attractive surface.³ An analysis of the singularity for Γ in Eq. (52)

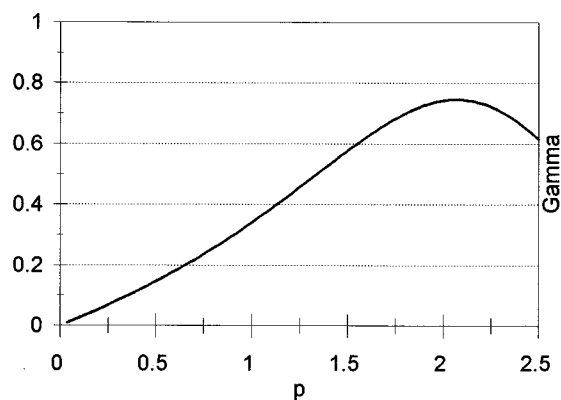


FIG. 5. Adsorption isotherm from van der Waals equation for $T = 1.4 T^*$.

gives $\Gamma \sim (1 - P/P_s)^{-1/2}$, where P_s is the saturation vapor pressure. This agrees with a recent model for polymolecular adsorption isotherms.¹⁰

Figure 5 presents an adsorption isotherm for $T^* = 1.4$. The shape of this curve corresponds to the behavior found for adsorption of a supercritical fluid.¹¹

CONCLUSION

The analogy of the integral in compressibility equation to the integral in Gibbs adsorption provides a new connection between two-dimensional and three-dimensional phenomena.

The Henry's law isotherm results in an expression for the second virial coefficient B_2 identical to the well-known result from statistical mechanics. The Langmuir isotherm leads to a new hard-sphere equation of state which is quite accurate. This equation can be written explicitly in either pressure or density. The Frumkin isotherm gives a new equation of state for the square-well fluid that has only one adjustable parameter and which fits computer simulation results with remarkable accuracy.

The adsorption isotherm can be represented as a function of density and, for example, Eq. (49) can be used to derive the van der Waals equation of state for a hard-sphere fluid.

The Ono-Kondo model of Gibbs adsorption results in the exact equation for the second virial coefficient of the square-well fluid.

Derivation of the adsorption isotherms from equations of state also is possible and gives interesting results. For example, the van der Waals equation gives a new adsorption isotherm that describes polymolecular adsorption for $T < T_c$ and which predicts the unusual adsorption isotherms observed for supercritical fluids. More complicated equations of state (like those for chain¹² or amphoteric molecules¹³) also could be used to get $\Gamma(P)$ from Eq. (6).

It is hoped that understanding this analogy will lead to a better understanding of how molecular behavior manifests itself in the equation of state and in adsorption phenomenon.

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