Adsorption from a one-dimensional lattice gas and the Brunauer–Emmett–Teller equation

(Ising model/reference system/Gibbs excess adsorption/Gibbs integral)

TERRELL L. HILL*

Laboratory of Molecular Biology, National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, MD 20892

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ABSTRACT   An exact treatment of adsorption from a one-dimensional lattice gas is used to eliminate and correct a well-known inconsistency in the Brunauer–Emmett–Teller (B.E.T.) equation—namely, Gibbs excess adsorption is not taken into account and the Gibbs integral diverges at the transition point. However, neither model should be considered realistic for experimental adsorption systems.

The well-known Brunauer–Emmett–Teller (B.E.T.) equation (Eq. **36** below) is used primarily to determine the surface area from the physical adsorption of a gas on a solid surface. The adsorbate model on which the equation is based (1) is an assembly of independent linear piles of adsorbed molecules (with no vacancies). The piles are in equilibrium with a dilute three-dimensional gas. Because the gas is dilute, no Gibbs reference-system correction is made.

In the actual adsorption of a gas on a solid surface, when the gas pressure is increased (at constant temperature) up to the vapor pressure of the corresponding liquid, the gas begins to condense to liquid and the adsorbate becomes bulk liquid on the solid surface. The Gibbs integral (see Eq. **17** below), up to the vapor pressure of the liquid, is finite and related to appropriate surface tensions. In the B.E.T. model, the dilute gas condenses to liquid at its vapor pressure but the independent linear piles of adsorbate molecules, though they become infinite in size, certainly do not become or resemble a liquid. This fundamental inconsistency in the B.E.T. model is reflected in the well-known divergence of the Gibbs integral in this case, which is unrealistic thermodynamically.

The objective of this paper is, in contrast to the B.E.T. model, to treat one-dimensional adsorption in a self-consistent way. This is accomplished by considering adsorption initiated by an attracting site at the end of a one-dimensional lattice gas. The adsorbate is then part of the lattice gas and in equilibrium with it. The B.E.T. equation is recovered as a close approximation in a special case, but the approximation does not hold at higher lattice gas densities: a finite Gibbs integral is always found from the exact treatment.

Yagov and Lopatkin (2, 3) have previously treated this model by a different method and have obtained, in a different form, the equivalent of Eq. **14** below. However, they did not discuss the main topics here: the B.E.T. equation as a limiting case of the general treatment; the rescue of the Gibbs integral from the B.E.T. divergence by use of the present self-consistent model; a discussion of the thermodynamic functions of the model; and consideration of a special case with interesting symmetry.

Neither the B.E.T. model nor the present model should be thought of as resembling, even slightly, experimental three-dimensional adsorption systems.

The model here has interesting properties quite aside from the B.E.T. connection. This is essentially the one-dimensional
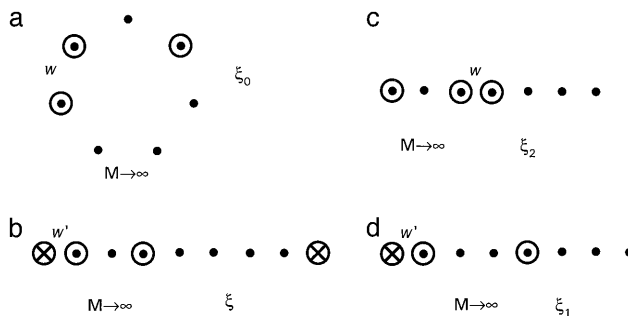

FIG. 1.   (*a*) Reference system: $M = 7$ sites in a circle; three sites are occupied by molecules. Nearest-neighbor occupied sites have an interaction energy w. ξ_0 is the grand partition function. (*b*) $M = 7$ sites with an adsorbent molecule $\otimes$ at each end. The interaction energy between $\otimes$ and an occupied adjacent site is w'. (*c*) $M = 7$ sites with two free ends (no adsorbent). (*d*) $M = 7$ sites with one free end and an adsorbent at the other end.

Ising problem with end effects, but it is the end effects that receive the focus of attention. We begin with the general derivation but return to the B.E.T. equation and the other topics mentioned in due course.

The Adsorption Model

We consider first, as a reference system, the one-dimensional Ising model in Fig. 1a. This is the lattice gas without adsorption and without ends. The number of sites is M ($M = 7$ in the figure), and the number of sites occupied by a molecule is N_0 ($N_0 = 3$ in the figure). We are interested here in large systems with $M \rightarrow \infty$. Nearest-neighbor molecules have an interaction energy w (Fig. 1a). A molecule on a site has partition function $q(T)$. The lattice gas is an open system (molecules go onto and off of sites) with thermodynamic variables μ (chemical potential), M, and T. We shall use the notation

$$x(\mu, T) = q\lambda = q(T)e^{\mu/kT}, \; \theta_0 = \bar{N}_0/M. \quad [1]$$

The variable x is an "activity," a convenient measure of the chemical potential at constant temperature. The subscript in Eq. **1** refers to the reference system.

The nearest-neighbor interaction parameter is $y \equiv e^{-w/kT}$. If $w = 0$ and $y = 1$, we have the simple and familiar relations

$$\theta_0 = \frac{x}{1+x}, \; x = \frac{\theta_0}{1-\theta_0}. \quad [2]$$

For attractive interactions, $w < 0$ and $y > 1$. A first-order phase transition does not occur (ref. 4, p. 333) in this one-dimensional system, even for very large y (e.g., at very low temperatures). However, by analogy with two- (simple square)

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and three- (simple cubic) dimensional lattice gases, where phase transitions occur at $\theta_0 = \frac{1}{2}$ when $T < T_c$, we can take $\theta_0 = \frac{1}{2}$ as locating a pseudo-transition point. The one-dimensional $\theta_0(x, y)$ is given below in Eq. **15**; $\theta_0 = \frac{1}{2}$ when $x = 1/y$. Incidentally, there are somewhat more elaborate one-dimensional lattice gas systems that *do* exhibit a first-order phase transition (5, 6).

In Fig. 1b, the lattice gas has a *permanent* adsorbent molecule $\otimes$ at each end. As indicated in the figure, the interaction energy between the adsorbent molecule and a first-row lattice gas molecule is w'. Any perturbation of q for a first-row molecule can be included in w'. Usually $w' < 0$ and $z \equiv e^{-w'/kT} > 1$. If $z > 1$ and especially if $z \gg 1$, extra lattice-gas molecules will tend to accumulate on the sites near $\otimes$ (the effect would be spatially propagated by $y > 1$, and especially by $y \gg 1$). This extra accumulation, or surface excess (Gibbs), represents the amount of adsorption. It is possible for the surface excess to be negative.

Let ξ be the grand partition function for the system in Fig. 1b, with variables μ, M, T (M is very large), and let ξ_0 be the grand partition function for the reference system (Fig. 1a) with the same μ, M, T. Then (ref. 4, p. 329)

$$\bar{N} - \bar{N}_0 = x\left(\frac{\partial \ln \xi/\xi_0}{\partial x}\right)_T \qquad [3]$$

is the extra accumulation of molecules at two ends and

$$\bar{N}_{\text{ex}} = \frac{\bar{N} - \bar{N}_0}{2} = x\left[\frac{\partial \ln(\xi/\xi_0)^{1/2}}{\partial x}\right]_T \qquad [4]$$

is the desired Gibbs surface excess (amount of adsorption) at one end. An alternative to the use of $(\xi/\xi_0)^{1/2}$ in Eq. **4** is to substitute (see Fig. 1) $\xi_1/\xi_2^{1/2}$ in place of $\xi^{1/2}$, where $\xi_2 = \xi_1(z = 1)$. Both methods yield the same result, though the second has less complicated algebra.

For the second method, we need to find ξ_0 and ξ_1. We use a standard matrix procedure for both. For ξ_0 (ref. 4, p. 325),

$$\xi_0 = \sum_{\nu_1, \ldots, \nu_M = 1}^{2} A(\nu_1, \nu_2)A(\nu_2, \nu_3) \cdots A(\nu_M, \nu_1)$$

$$= \text{Tr}\mathbf{A}^M = \gamma_1^M + \gamma_2^M, \qquad [5]$$

where

$$\mathbf{A} = \begin{pmatrix} 1 & x \\ 1 & xy \end{pmatrix} \qquad [6]$$

and γ_1 and γ_2 are the two eigenvalues of $\mathbf{A}$,

$$\gamma_1, \gamma_2 = \frac{1 + xy \pm [(1 - xy)^2 + 4x]^{1/2}}{2}, \qquad [7]$$

with $\gamma_1 > \gamma_2$. Because $M \to \infty$, $\xi_0 = \gamma_1^M$.

For ξ_1 (ref. 4, p. 339),

$$\xi_1 = \sum_{\nu_1, \ldots, \nu_M = 1}^{2} r(\nu_1)A(\nu_1, \nu_2) \cdots A(\nu_{M-1}, \nu_M)c(\nu_M)$$

$$= \sum_{\nu_1, \ldots, \nu_M = 1}^{2} r(\nu_1)A^{M-1}(\nu_1, \nu_M)c(\nu_M), \qquad [8]$$

where

$$\mathbf{r} = (1, zx), \quad \mathbf{c} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}. \qquad [9]$$

After a similarity transformation (ref. 4, p. 339), we find (using $M \to \infty$)

$$\xi_1 = \frac{\gamma_1^{M-1}(1 + x - \gamma_2)(1 - z + z\gamma_1)}{\gamma_1 - \gamma_2} \qquad [10]$$

$$\frac{\xi_1}{\xi_0} = \frac{(1 + x - \gamma_2)(1 - z + z\gamma_1)}{\gamma_1(\gamma_1 - \gamma_2)} \qquad [11]$$

$$\frac{\xi_2}{\xi_0} = \frac{1 + x - \gamma_2}{\gamma_1 - \gamma_2} \qquad [12]$$

$$\left(\frac{\xi}{\xi_0}\right)^{1/2} = \frac{\xi_1}{\xi_0}\left(\frac{\xi_0}{\xi_2}\right)^{1/2} = \frac{(1 + x - \gamma_2)^{1/2}(1 - z + z\gamma_1)}{\gamma_1(\gamma_1 - \gamma_2)^{1/2}}. \qquad [13]$$

Finally, from Eq. **4**,

$$\bar{N}_{\text{ex}} = \frac{x}{2\sqrt{\ }}\left[\frac{(2 - y)\sqrt{\ } + u}{2(1 + x - \gamma_2)} + \frac{z(y\sqrt{\ } + u)}{1 - z + z\gamma_1} - \frac{y\sqrt{\ } + u}{\gamma_1} - \frac{u}{\sqrt{\ }}\right]$$

$$u \equiv xy^2 - y + 2, \quad \gamma_1 - \gamma_2 = \sqrt{\ } = [(1 - xy)^2 + 4x]^{1/2}. \qquad [14]$$

Also, for the reference system, because $\xi_0 = \gamma_1^M$,

$$\theta_0 = \frac{\bar{N}_0}{M} = x\left(\frac{\partial \ln \gamma_1}{\partial x}\right)_T = \frac{x(y\sqrt{\ } + u)}{2\sqrt{\ }\gamma_1} = \frac{2x}{\sqrt{\ }(1 - xy + \sqrt{\ })}. \qquad [15]$$

There are two Gibbs integrals of particular interest for this model:

$$\int_0^\infty \frac{\bar{N}_{\text{ex}}}{x} dx = \int_{x=0}^{x=\infty} d\ln\left(\frac{\xi}{\xi_0}\right)^{1/2} = \ln\left(\frac{\xi}{\xi_0}\right)^{1/2}\Big|_{x=0}^{x=\infty} = \ln\frac{z}{y^{1/2}} \qquad [16]$$

$$\int_0^\infty \frac{\bar{N}_{\text{ex}}}{x} dx = \ln\left(\frac{\xi}{\xi_0}\right)^{1/2}\Big|_{x=0}^{x=1/y} = \ln\frac{y^{1/2} + z}{[2y^{1/2}(1 + y^{1/2})]^{1/2}}. \qquad [17]$$

The lower limit does not contribute. Both integrals are finite. The second is significant because $x = 1/y$ locates the pseudo-transition point, as mentioned above.

Excess Thermodynamic Functions

Because we have been discussing a single one-dimensional lattice gas chain of sites, the thermodynamics of small systems (7) could be used here. However, since the appropriate adsorption thermodynamic formulation is already available (ref. 8, pp. 252–253), we use this alternative approach.

We consider a surface with B adsorbent molecules, from each of which a lattice gas chain of M sites extends vertically. M and B are both large. Molecules at chemical potential μ go on and off of the sites. The chains are independent of each other. The total number of lattice sites is MB (a "volume") and the mean total number of occupied sites is $\bar{N}_a$. The basic thermodynamic relations for this system are (ref. 8, pp. 252–253)

$$dE_a = TdS_a - \Phi d(MB) - \varphi dB + \mu d\bar{N}_a \qquad [18]$$

$$E_a = TS_a - \Phi MB - \varphi B + \mu\bar{N}_a. \qquad [19]$$

The adsorbent molecules merely present an external field; they are not included in the thermodynamic functions.

The reference system consists of the same MB sites but with no adsorbent molecules present. The lattice gas chemical potential is again μ and mean properties of the reference

system extend right up to the surface (no end effects; compare Fig. 1a). For the reference system, then,

$$dE_g = TdS_g - \Phi d(MB) + \mu d\bar{N}_g \qquad [20]$$

$$E_g = TS_g - \Phi MB + \mu \bar{N}_g. \qquad [21]$$

On subtracting Eqs. **20** and **21** from Eqs. **18** and **19** (e.g., $E \equiv E_a - E_g$), we obtain relations among the Gibbs excess functions:

$$dE = TdS - \varphi dB + \mu d(\bar{N}_{ex}B) \qquad [22]$$

$$E = TS - \varphi B + \mu \bar{N}_{ex}B. \qquad [23]$$

The physical significance of φ is a "spreading pressure," tending to increase B.

From Eqs. **22** and **23** we deduce

$$\bar{N}_{ex}d\mu = -(S/B)dT + d\varphi. \qquad [24]$$

At constant T, $d\mu = kTd\ln x$. Then (see Eq. **16**)

$$d\varphi = kT\bar{N}_{ex}d\ln x \quad (T \text{ constant}) \qquad [25]$$

$$\varphi(x) = kT \int_0^x \bar{N}_{ex}(x')d\ln x' = kT\ln\left[\frac{\xi(x)}{\xi_0(x)}\right]^{1/2}. \qquad [26]$$

Thus Eq. **13** gives an explicit expression for $\varphi(x)$ and, of course, Eq. **14** provides $\bar{N}_{ex}(x)$.

To obtain S/B and E/B, we use Eq. **24**:

$$\frac{S}{B} = \left(\frac{\partial\varphi}{\partial T}\right)_\mu = \left(\frac{\partial\varphi}{\partial x}\right)_T\left(\frac{\partial x}{\partial T}\right)_\mu + \left(\frac{\partial\varphi}{\partial T}\right)_x. \qquad [27]$$

Eq. **25** gives $(\partial\varphi/\partial x)_T$ and $(\partial x/\partial T)_\mu$ follows easily from Eq. **1**. A fairly long calculation (taking w and w' as constants), using Eqs. **13** and **26**, yields $(\partial\varphi/\partial T)_x$. The final result is

$$S/B = (E/BT) + (\varphi/T) - (\mu\bar{N}_{ex}/T), \qquad [28]$$

where

$$\frac{E}{B} = \bar{N}_{ex}kT^2\frac{d\ln q}{dT} + \frac{1}{2\sqrt{}}\left[\frac{xyw(\gamma_2-1)}{1+x-\gamma_2}\right.$$

$$\left. + \frac{2z(w'\sqrt{} + xyw)(\gamma_1-1)}{1-z+z\gamma_1} - \frac{2xyw(\gamma_1-1)}{\gamma_1} + \frac{xy(1-xy)w}{\sqrt{}}\right].$$

$$[29]$$

The terms in w and w' arise from nearest-neighbor or adsorbent interactions. The w' term has a simple interpretation because the reference system has no w' interactions. Thus, the coefficient of w' gives θ_1, the probability that the first-row site in the adsorption system is occupied:

$$\theta_1 = \frac{z(\gamma_1-1)}{1-z+z\gamma_1}. \qquad [30]$$

The coefficient of w gives the mean number of *excess w* interactions in the adsorption system.

The general θ_i can be found as follows. Replace q for the row i site by $q\varepsilon$. The matrix procedure can be generalized to give $\xi_1(\varepsilon)$. Then $\theta_i = \varepsilon\partial\ln\xi_1(\varepsilon)/\partial\varepsilon$ at $\varepsilon = 1$. The factor ε counts row i occupancy. One finds ($i \geq 2$)

$$\theta_i = \frac{x(\gamma_1^{i-1} - \gamma_2^{i-1}) + zx[(\gamma_1^i - \gamma_2^i) - (\gamma_1^{i-1} - \gamma_2^{i-1})]}{(\gamma_1 - \gamma_2)\gamma_1^{i-2}(1 + x - \gamma_2)(1 - z + z\gamma_1)}. \qquad [31]$$

If $i \to \infty$, $\theta_i \to \theta_0$. If $y = 1$, $\theta_i = x/(1 + x)$ for $i \geq 2$. Eq. **31** is also correct for $i = 1$.

The following sum is easy to perform:

$$\bar{N}_{ex} = \sum_{i=1}^\infty (\theta_i - \theta_0)$$

$$= \frac{\gamma_1^2 x(z - 1 - z\gamma_2)}{(\gamma_1 - \gamma_2)^2(1 + x - \gamma_2)(1 - z + z\gamma_1)}. \qquad [32]$$

This is a third equivalent expression for $\bar{N}_{ex}$.

Relation to the B.E.T. Equation

To simulate the B.E.T. model we need very large y (low temperature) to eliminate almost all vacancies in the adsorption lattice gas pile of molecules. Also, the pseudo-transition point is $x = 1/y$, or $xy = 1$. Thus, xy here corresponds to x in the B.E.T. equation (where $x = 1$ is the transition point). Further, here at very small x, $\bar{N}_{ex} = [(z - 1)/y]xy$. Because cx is the corresponding B.E.T. expression, c corresponds to $(z - 1)/y$ here. Ordinarily c is of order 10 or 100; hence z is even larger than y. Thus, $c \leftrightarrow z/y$. In summary,

$$\text{B.E.T. } x \leftrightarrow xy, \ c \leftrightarrow z/y, \ cx \leftrightarrow zx. \qquad [33]$$

We now consider Eq. **14** for $\bar{N}_{ex}$ with y and z both very large. Because $xy = O(1)$, $x \ll 1$. Hence, we use the following expansions:

$$\sqrt{} = 1 - xy + \frac{2x}{1-xy} + \cdots, \ \gamma_1 = 1 + \frac{x}{1-xy} + \cdots$$

$$\gamma_2 = xy - \frac{x}{1-xy} + \cdots, \ 1 - z + z\gamma_1 = 1 + \frac{zx}{1-xy} + \cdots.$$

$$[34]$$

If we write the four terms in [ ] in Eq. **14** as $A' + B' - C' - D'$, we then find

$$A' = D' = \frac{xy^2 - y}{1 - xy}, \ C' = \frac{2}{1-xy}, \ B' = \frac{2z}{1 - xy + zx}. \qquad [35]$$

Thus, only B' contributes significantly. Then

$$\bar{N}_{ex} \cong \frac{xB'}{2\sqrt{}} \cong \frac{zx}{(1-xy)(1-xy+zx)}. \qquad [36]$$

The same result follows in similar fashion from ref. 2 or ref. 3. In view of the correspondences in **33**, this is the familiar B.E.T. equation.

Table 1 refers to the case $y = 10^3$, $z = 2 \times 10^5$, B.E.T. $c = z/y = 200$. Fig. 2 shows, for this case, $\bar{N}_{ex}$ from Eqs. **14** and **36**, as functions of xy. Also included in the figure is $\theta_0(xy)$, Eq. **15**, for $y = 10^3$. It is seen from the table and the figure that the B.E.T. approximation to $\bar{N}_{ex}$ is adequate in this case up to about $xy = 0.75$. As mentioned at the outset, the B.E.T.

Table 1. The B.E.T. approximation with $y = 10^3$, $z = 2 \times 10^5$

xy	$\bar{N}_{ex}$ (exact)	$xB'/2\sqrt{}$ (exact)	Eq. **36** (B.E.T.)
0.1	1.063	1.063	1.063
0.2	1.225	1.225	1.225
0.4	1.650	1.652	1.654
0.6	2.468	2.477	2.492
0.8	4.733	4.824	4.994
0.9	8.025	8.641	9.994
1.0	8.153	16.309	∞

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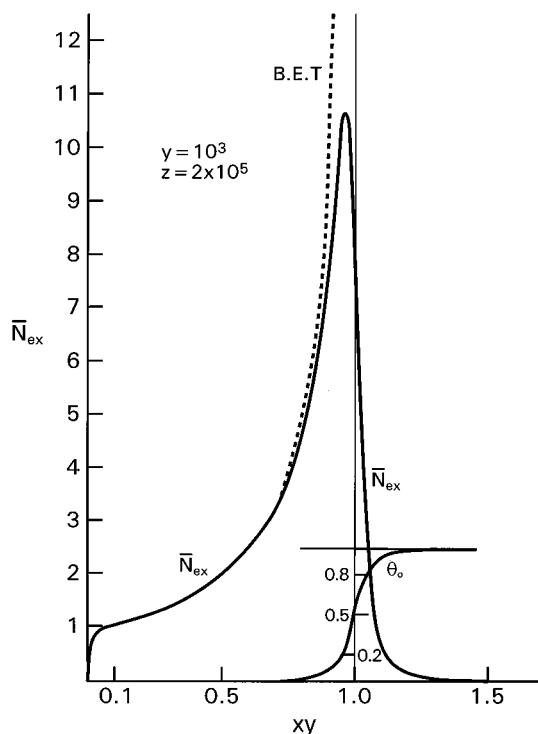*Proc. Natl. Acad. Sci. USA 93 (1996)*   14331

FIG. 2. The solid curve labeled $\bar{N}_{ex}$ is the case $y = 10^3$, $z = 2 \times 10^5$, plotted against xy. The dashed curve labeled B.E.T. is an approximation. The solid curve labeled θ_0 (different scale) is $\theta_0(xy)$ for the reference system with $y = 10^3$.

equation does not include a Gibbs reference system correction. The reference system here, for self-consistency, is the one-dimensional Ising model (Fig. 1a). The B.E.T. omission of a Gibbs correction is appropriate in the present model so long as $\theta_0(xy)$ (Fig. 2) is negligible. Above $xy \cong 0.75$, θ_0 is not negligible: Eqs. **14** and **36** differ significantly. Note that the exact $\bar{N}_{ex} \to 0$ as $\theta_0 \to 1$ (at $xy > 1$). This is to be expected because the introduction of adsorbent can hardly *add* molecules to an already virtually saturated reference system; hence, $\bar{N}_{ex} \to 0$. (However, if z is small, the adsorbent can still *subtract* molecules when $\theta_0 \to 1$.)

The shape of the $\bar{N}_{ex}(xy)$ curve in Fig. 2 resembles qualitatively experimental supercritical Gibbs excess adsorption isotherms (9). This is not surprising because any finite $y > 1$ in the one-dimensional lattice gas model corresponds to $T > T_c$ ($T_c = 0$ K): all $\bar{N}_{ex}$ curves are supercritical.
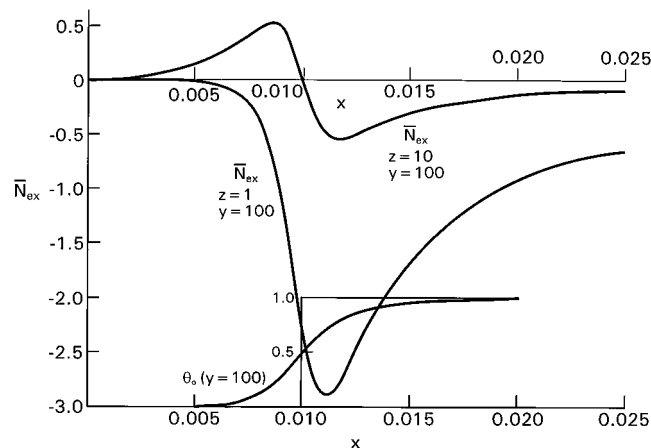

FIG. 3. The two upper curves are $\bar{N}_{ex}(x)$ for $z = 10$, $y = 100$ and $z = 1$, $y = 100$. The lowest curve is $\theta_0(x)$ (different scale) for $y = 100$.

If y is increased (beyond 10^3) along with z in the same ratio ($c = z/y$), the θ_0 curve in Fig. 2 becomes steeper at $\theta_0 = \frac{1}{2}$ (the slope is $y^{1/2}/4$) so that the B.E.T. approximation would be adequate for larger xy, and the $\bar{N}_{ex} \to 0$ approach would occur at smaller xy.

The Gibbs integrals using the exact $\bar{N}_{ex}$, Eqs. **16** and **17**, are finite. The B.E.T. Gibbs integral to $xy = 1$ diverges because of the factor $(1 - xy)^{-1}$ in Eq. **36**. For large y and z, the integral in Eq. **17** is approximately $\ln[z/(2y)^{1/2}]$.

In an experimental physical adsorption system at $T < T_c$, $\bar{N}_{ex} \to \infty$ as $p \to p_0$ (vapor pressure), but the Gibbs integral to p_0 is finite.

The interaction (w, w') part of E/B in Eq. **29** becomes, in the B.E.T. special case, using Eqs. **34**,

$$\frac{E_{ww'}}{B} = \frac{zxw'}{1 - xy + zx} + \frac{zx \cdot xyw}{(1 - xy)(1 - xy + zx)}. \quad [37]$$

The coefficient of w' is the expected B.E.T. θ_1 and the coefficient of w can be shown to be the B.E.T. mean number of first-neighbor pairs in a pile.

Other Special Cases

The interested reader will find it easy to examine special cases of Eq. **14** either analytically or by computer-generated curves. I mention only a few examples below. Also, Yagov and Lopatkin (2) show some curves in the form $\bar{N}_{ex}(\theta_0)$, using $\theta_0(x)$ to eliminate x.

From Eq. **16** we note that the complete Gibbs integral is zero if $z = y^{1/2}$. Also, Eq. **14** yields $\bar{N}_{ex} = 0$ if we put $z = y^{1/2}$ and $x = 1/y$. Fig. 3 includes $\bar{N}_{ex}(x)$ for the particular case $z = 10$, $y = 100$. This curve, and others with $z = y^{1/2}$, suggest the symmetry property $\bar{N}_{ex}(x) = -\bar{N}_{ex}(1/xy^2)$ or $\bar{N}_{ex}(xy) = -\bar{N}_{ex}(1/xy)$. It is easy to deduce the zero Gibbs integral from the symmetry property. Further, the symmetry property has been confirmed using Eq. **32**. Also, from Eq. **31**, $\theta_i(x) + \theta_i(1/xy^2) = 1$ for all i; $\theta_i(1/y) = \frac{1}{2}$.

If $y = 1$, the sites are independent of each other. Eq. **14** reduces in this case to

$$\bar{N}_{ex} = \frac{zx}{1 + zx} - \frac{x}{1 + x} = \theta_1 - \theta_0. \quad [38]$$

The only contribution is from the first row.

When $z = 1$, the adsorbent is, in effect, removed. When $z = 0$, the first-row site is empty ($\theta_1 = 0$); the remainder of the chain (rows 2, 3, . . .) behaves like a full $z = 1$ chain. Thus,

$$\bar{N}_{ex}(z = 0) = \theta_1 - \theta_0 + \bar{N}_{ex}(z = 1) = -\theta_0 + \bar{N}_{ex}(z = 1). \quad [39]$$

This can be confirmed from Eq. **14**. Fig. 3 includes $\bar{N}_{ex}(x)$ for $z = 1$, $y = 100$.

When $y = 0$ (nearest-neighbor sites cannot be occupied), one finds from Eqs. **14** and **15** that, as $x \to \infty$, $\theta_0 \to \frac{1}{2}$ and $\bar{N}_{ex} \to \frac{1}{4}$.

When y and z are both large (as in B.E.T.), $\bar{N}_{ex} \cong y^{1/2}/4$ at $x = 1/y$.

Some expansions at small x:

$$\bar{N}_{ex} = (z - 1)x + (4 - 3y - 2z + 2zy - z^2)x^2 + \cdots$$

$$\theta_0 = x + (2y - 3)x^2 + \cdots$$

$$\theta_1 = zx + (-z + zy - z^2)x^2 + \cdots \quad [40]$$

$$\theta_2 = x + (-2 + y - z + zy)x^2 + \cdots.$$

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