PHYSICAL REVIEW E VOLUME 51, NUMBER 2 FEBRUARY 1995

Adsorption kinetics of hard disks from virial coefficients

Douglas Poland
Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

(Received 8 August 1994; revised manuscript received 19 October 1994)

We use the known values of the equilibrium virial coefficients through the eighth term for a two-dimensional fluid of hard disks to treat the reversible adsorption of disks from a gas of constant activity onto a surface. Assuming rapid equilibration on the surface, the virial series can be converted into a series for the time required to achieve a given degree of surface coverage. We then use the maximum-entropy method to extend the series, thus giving an approximate description of the entire time course of the adsorption process.

PACS number(s): 05.20.−y, 05.50.+q, 05.70.Jk, 05.70.Ln

INTRODUCTION

The cooperative adsorption of particles to a surface has recently been reviewed by Evans [1]. When the motion of molecules on the surface is rapid relative to the rate of adsorption one can use the equilibrium surface activity to describe the kinetics [2]. This method has been applied to models where the surface is a two-dimensional lattice, specifically to the adsorption of dimers [3], macromolecules [4], and to particles with nearest-neighbor attraction [5]. The method is also applicable to the adsorption of particles on a continuous surface. Recently van Rensburg [6] has pushed the virial series for hard disks through the eighth-term (B_8) and here we want to use this equilibrium series to describe the reversible kinetics of the adsorption of disks, the only cooperative interaction being the effect of excluded volume. We will use the exact equation of state for rods as a comparison test for the accuracy of the approach.

The eight term virial series for the pressure of hard disks in two dimensions can be turned into a similar series for the time required to achieve a given density of coverage of a surface. One standard method to extend such series is the use of rational approximants such as Padé approximants. Wang, Mead, and deLlano [7] have recently applied the maximum-entropy method to the extrapolation of power series, transforming the moment problem into a series problem via an appropriate integral. Here we will apply the maximum-entropy method to the extrapolation of the time dependence of the adsorption process. We begin by reviewing the basic kinetic equations for the adsorption of hard particles from a gas onto a surface.

I. BASIC KINETICS

We will assume that we have a smooth surface in contact with a gas of disks that is held at constant activity as illustrated in Fig. 1. The disks will adsorb reversibly to the surface, there being no interaction between the disks on the surface other than the requirement that they do not overlap on the surface. We will let z_g be the constant activity of the gas molecules, ρ_s be the density of molecules on the surface, and ρ_x the density of surface sites large enough to accommodate a disk. The basic adsorption and desorption processes are illustrated in Fig. 2 for the case of hard rods (for simplicity) which can also be thought of as a cross section describing the adsorption of disks. The net rate of the change of the density of molecules on the surface is the difference between the rate of adsorption and the rate of desorption

$$d\rho_s/dt = (\text{rate of adsorption}) - (\text{rate of desorption}) . \tag{1.1}$$

The adsorption process requires a gas molecule and a site on the surface large enough to fit a disk. The probability that a gas molecule is in a given volume element is proportional to the activity of the gas z_g and hence the rate of adsorption is proportional to the product of the gas activity and the density of surface sites ρ_x. The rate of desorption is simply proportional to the density ρ_s of surface molecules. Taking the proportionality constants (rate constants) for adsorption and desorption as k^+ and k^-, respectively, we have the two rates

$$\begin{aligned} &\text{rate of adsorption} = k^+[z_g^*][\rho_x] , \\ &\text{rate of desorption} = k^-[\rho_s] . \end{aligned} \tag{1.2}$$

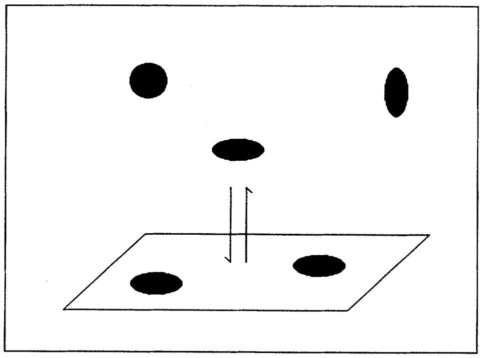


FIG. 1. Schematic illustration of the adsorption of disks from the gas phase onto a smooth surface.

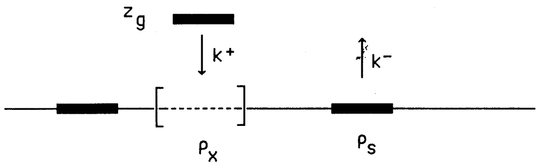


FIG. 2. Illustration of the adsorption and desorption processes for rods onto a one-dimensional surface. The rate of adsorption is proportional to z_g, the activity of molecules in the gas phase, and to ρ_x, the density of sites on the surface large enough to accommodate a molecule with rate constant k^+. The rate of desorption is proportional to ρ_s, the density of molecules on the surface with rate constant k^-.

We will use a star superscript, as on z_g^*, to indicate a constant quantity.

The chemical potentials and activities of molecules in the gas phase and adsorbed on the surface are

$$\beta\mu_g = \beta\mu_g^0 + \ln z_g , \quad \beta\mu_s = \beta\mu_s^0 + \ln z_s , \tag{1.3}$$

where $\beta = 1/kT$. The standard chemical potentials

$$\beta\mu_g^0 = -\ln q_g , \quad \beta\mu_s^0 = -\ln q_s , \tag{1.4}$$

can be expressed in terms of the internal partition functions q_g and q_s for gas and surface molecules, respectively. At equilibrium (at fixed temperature)

$$\beta\mu_g = \beta\mu_s \tag{1.5}$$

and

$$\frac{z_s^*}{z_g^*} = \frac{q_s}{q_s} = K = \frac{k^+}{k^-} . \tag{1.6}$$

The relation of (1.6) is equivalent to the condition

$$z_s^* = K z_g^* , \tag{1.7}$$

where K is the binding constant of the particles to the surface. Thus the final equilibrium surface activity z_s^* is simply proportional to the constant activity of the gas z_g^*.

To achieve a working relation we divide through on both sides of (1.1) by k^- and define a new time scale

$$t' = k^- t , \tag{1.8}$$

giving

$$d\rho_s/dt' = z_s^* \rho_x - \rho_s . \tag{1.9}$$

The quantity z_s^* in (1.9) is the constant equilibrium value of the surface activity given in (1.7). There are two variables (densities) in (1.9), ρ_s (the density of adsorbed molecules) and ρ_x (the density of proper adsorption sites). In order to integrate (1.9) we must know how ρ_x depends on ρ_s. If the motion of the particles on the surface (surface diffusion) is much faster than the rate of adsorption, then the surface states will be in an instantaneous state of internal equilibrium as the slow adsorption process occurs. In this case we can use the equilibrium relation between ρ_x, the density of vacancies on the surface large enough to accommodate a particle, and ρ_s the density of particles on the surface. This relation is obtained simply by setting $d\rho_s/dt' = 0$ in (1.9) giving a fundamental relation valid for all hard particle systems (not just two-dimensional adsorption models)

$$\rho_x = \rho_s / z_s . \tag{1.10}$$

We can now use (1.10) for ρ_x in (1.9), dropping the subscript s, understanding that ρ and z now refer to the surface density and activity. We obtain

$$\frac{d\rho}{dt'} = z^* \frac{\rho}{z} - \rho , \tag{1.11}$$

where z^* is the final equilibrium activity of the surface (determined by the constant activity of the gas in contact with the surface) and z is a time dependent surface activity. To use (1.11) we must know how the activity depends on the density, i.e.,

$$z = z(\rho) , \tag{1.12}$$

and this information comes from equilibrium statistical mechanics through virial series, which we review next.

II. ACTIVITY AND VIRIAL COEFFICIENTS

The virial equation of state gives the pressure as a series in the density

$$\beta p/\rho = 1 + \sum_{n=1}^{\infty} B_{n+1} \rho^n . \tag{2.1}$$

In general, the virial coefficients B_n are functions of temperature, but for hard particles they are constants. From the basic thermodynamic equation for the chemical potential

$$d\mu = \frac{1}{\rho} \frac{\partial p}{\partial \rho} d\rho \tag{2.2}$$

we can use (2.1) and integrate (2.2) term by term to obtain μ [with μ^0 being an integration constant given by (1.4)]. We then use the general relation of (1.3) between the chemical potential and the activity to obtain

$$z = \rho \exp \left[\sum_{n=1}^{\infty} \left[\frac{n+1}{n} \right] B_{n+1} \rho^n \right] , \tag{2.3}$$

which gives the activity in terms of the density and the virial coefficient, which is the relation indicated symbolically in (1.12) that is required to give the basic rate equation (1.11) in terms of the single variable ρ. The quantity that appears in (1.11) is the ratio of the activity to the density which is the activity coefficient

$$\gamma(\rho) = z/\rho . \tag{2.4}$$

It is conventional to write the B_n relative to B_2. We use the standard symbol

$$b = B_2 , \tag{2.5}$$

and define relative virial coefficients

$$B_{n+1}' = B_{n+1}/b^n . \tag{2.6}$$

It is also useful to express the density relative to the density at close-packing ρ_m. For this purpose we introduce the variable

$$r = \rho/\rho_m . \tag{2.7}$$

Using (2.4), (2.6), and (2.7) we can express the density dependence of the activity as

$$\ln\gamma(r)=\sum_{n=1}^{\infty}\left[\frac{n+1}{n}\right]B_{n+1}(b\rho_m)^n r^n \ . \tag{2.8}$$

For rods (where σ is the length of the rod) we have

$$b=\sigma,\quad \rho_m=1/\sigma,\quad (b\rho_m)=1 \ , \tag{2.9}$$

while for disks (where σ is the diameter of the disk)

$$b=\frac{\pi}{2}\sigma^2,\quad \rho_m=\frac{2}{\sqrt{3}}\frac{1}{\sigma^2},\quad (b\rho_m)=\frac{\pi}{\sqrt{3}} \ . \tag{2.10}$$

The equation of state for rods is known exactly [10,11]

$$\beta_p/\rho=\frac{1}{1-\sigma\rho} \ , \tag{2.11}$$

with

$$B_{n+1}=\sigma^n \ . \tag{2.12}$$

In this case we have a closed expression for the activity as a function of the density

$$z=\left[\frac{\rho}{1-\sigma\rho}\right]\exp\left[\frac{\sigma\rho}{1-\sigma\rho}\right] , \tag{2.13}$$

which we can also write in terms of the activity coefficient of (2.4) and the relative density of (2.7)

$$\gamma=\left[\frac{1}{1-r}\right]\exp\left[\frac{r}{1-r}\right] \ . \tag{2.14}$$

For comparison with the series for disks, the beginning terms in the series expansion of the logarithm of the above expression are

$$\ln\gamma=2r\left[1+\tfrac{3}{4}r+\tfrac{2}{3}r^2+\tfrac{5}{8}r^3+\tfrac{3}{5}r^4+\tfrac{7}{12}r^5+\tfrac{4}{7}r^6+\cdots\right] . \tag{2.15}$$

For disks the B_n are known exactly through B_4 and have been determined numerically through B_8 by van Rensburg [6]; this reference lists the earlier work on the numerical determination of B_5–B_7. The exact results are

$$\begin{aligned} B_2&=b=\frac{\pi}{2}\sigma^2 \ ,\\ B_3/b^2&=\tfrac{4}{3}-\frac{\sqrt{3}}{\pi} \ ,\\ B_4/b^3&=2-\frac{9\sqrt{3}}{2\pi}+\frac{10}{\pi^2} \ , \end{aligned} \tag{2.16}$$

while the numerical values are (giving the uncertainties in the final digits in parentheses)

$$\begin{aligned} B_5/b^4&=0.333\,556\,04(4) \ ,\\ B_6/b^5&=0.198\,83(1) \ ,\\ B_7/b^6&=0.114\,859(70) \ ,\\ B_8/b^7&=0.065\,140(80) \ . \end{aligned} \tag{2.17}$$

These numbers yield the following series for $\ln\gamma$ for disks

$$\begin{aligned} \ln\gamma=(3.6276)r\,[1&+(1.063\,81)r+(1.167\,29)r^2\\ &+(1.244\,02)r^3+(1.291\,06)r^4\\ &+(1.315\,85)r^5+(2.324\,62)r^6\\ &+\cdots] \ . \end{aligned} \tag{2.18}$$

We require this series for two reasons. First, we need to use it in our basic kinetic equation given by (1.11) to give z (or γ) as a function of ρ (or r) and, second, we need to know the equilibrium value γ^* corresponding to the equilibrium value r^* (measuring the equilibrium fraction of coverage).

For numerical examples we will take the following values of the required parameters. For rods we pick the final state that is half of the close-packed density

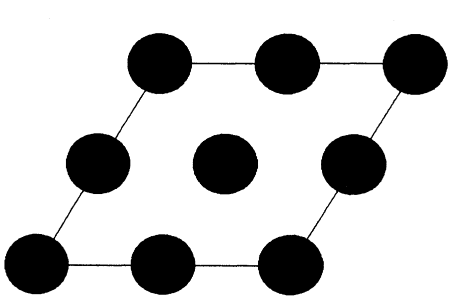
$$r^*=1/2,\quad \gamma^*=2e\ \ (\text{rods}) \ . \tag{2.19}$$

The value of γ^* given above that corresponds to $r^*=\frac{1}{2}$ is obtained from the exact relation of (2.14). For disks we pick a value of r^* that is the two-dimensional analog of $r^*=\frac{1}{2}$ for the one-dimensional case, namely, $r^*=\frac{1}{4}=(\frac{1}{2})^2$. Thus

$$r^*=\tfrac{1}{4},\quad \gamma^*=3.452\,779\ \ (\text{disks}) \ . \tag{2.20}$$

In this case we have used a Padé approximant to the series for $\ln\gamma$ given in (2.18) to calculate the required value of γ^*. When we similarly use a Padé approximant to the series of (2.15) for the case of rods we obtain the exact value to six figures. The equilibrium densities indicated above for rods and disks are illustrated in Fig. 3 (shown as a regular pattern for simplicity).

Rods (r* = 1/2)



Disks (r* = 1/4)

FIG. 3. Illustration of the final, equilibrium densities for rods and disks that will be used in our numerical examples. In both cases r^* is the density relative to close packing. A regular arrangement is shown for simplicity.

III. SERIES SOLUTION FOR THE KINETIC EQUATION

In the preceding section we reviewed how the activity can be expressed as a function of the density using virial coefficients. We can now proceed to express the solution of the kinetic equation as a series in the density. We introduce one final variable, the ratio of the time-dependent density to the final equilibrium density

$$x=\rho/\rho^* \ . \tag{3.1}$$

This variable ranges from zero to one as the time varies from zero to infinity (assuming no coverage of the surface at zero time). With this change of variable (1.11) becomes

$$\frac{dx}{dt'}=\frac{\gamma^*}{\gamma(x)}-x \ , \tag{3.2}$$

where γ^* is the constant equilibrium value of γ (determined by the constant activity of the gas) and $\gamma(x)$ is the time-dependent activity coefficient of the surface. We now express γ in terms of the variable x rather than in terms of the variable r used previously. The change in variable is accomplished by the relation

$$r=r^*x \ , \tag{3.3}$$

where r^* is the fraction of close-packing at the equilibrium state.

It is convenient to divide all the terms in (3.2) by γ^* giving

$$\frac{dx}{dt''}=\frac{1}{\gamma(x)}-\frac{1}{\gamma^*}x \ , \tag{3.4}$$

with

$$t''=t'\gamma^* \ . \tag{3.5}$$

Finally we drop the primes on t giving

$$\frac{dx}{dt}=\frac{1}{\gamma(x)}-\frac{1}{\gamma^*}x \ , \tag{3.6}$$

where

$$\gamma(x)=1+c_1x+c_2x^2+\cdots \ , \tag{3.7}$$

as given by (2.15) for rods and (2.18) for disks (as the logarithm of γ).

We can then formally integrate (3.6)

$$\int_0^x \frac{\gamma(w)}{1-w\gamma(w)/\gamma^*}dw=t \ . \tag{3.8}$$

Using the series form of (3.7) we can expand the quantity in the integral and integrate term by term giving a series solution of the form

$$t=x\left[1+\sum_{n=1}^{\infty}A_nx^n\right] \ , \tag{3.9}$$

giving the time required to produce a given fraction of the final density as a series in that fraction. Thus a finite number of virial coefficients (the B_n) gives a finite number of coefficients (the c_n) in the expansion for $\gamma(x)$ of (3.7), which in turn gives a finite number of coefficients (the A_n) in the series for t of (3.9). Given the virial coefficients for disks through B_8 gives the coefficients in the above equation through A_7.

For the conditions listed in (2.19) and (2.20) of $r^*=\frac{1}{2}$ for rods and $r^*=\frac{1}{4}$ for disks (illustrated in Fig. 3) the series of (3.9) gives, for rods,

$$\begin{aligned} t/x=1&+(0.591\,970)x+(0.425\,571)x^2\\ &+(0.330\,473)x^3+(0.268\,620)x^4\\ &+(0.225\,442)x^5+(0.193\,822)x^6\\ &+(0.169\,80)x^7+\cdots \ , \end{aligned} \tag{3.10}$$

and for disks,

$$\begin{aligned} t/x=1&+(0.598\,43)x+(0.420\,81)x^2+(0.319\,794)x^3\\ &+(0.256\,41)x^4+(0.213\,673)x^5+(0.183\,11)x^6\\ &+(0.160\,204)x^7+\cdots \ . \end{aligned} \tag{3.11}$$

The two series are very similar and are very well behaved.

We now move on to methods for extending the series, in particular the maximum-entropy method. For future reference, we note that we can obtain the exact solution for rods by numerically integrating the following form (for $r^*=\frac{1}{2}$)

$$t=\int_0^x \frac{dw}{(1-w/2)\exp[-w/(2-w)]-w/2e} \ . \tag{3.12}$$

IV. MAXIMUM-ENTROPY METHOD

We will follow the treatment of the maximum-entropy method given by Mead and Papanicolaou [8]. Given an unknown distribution function $P(x)$ with moments (not chemical potentials)

$$\mu_n=\int_a^b x^nP(x)dx \ , \tag{4.1}$$

which are known for $n=0$ to $n=N$, the maximum-entropy, or least-biased, approximation to $P(x)$ is given by

$$P_N(x)=\exp[-\Gamma_N(x)] \ , \tag{4.2}$$

where

$$\Gamma_N(x)=\sum_{n=0}^{N}\lambda_nx^n \ , \tag{4.3}$$

where the $(N+1)$ λ's are determined to give the correct $(N+1)$ μ's. Mead and Papanicolaou [8] have proved that the series of functions $P_N(x)$ approach the correct $P(x)$ as $N\to\infty$. For a distribution defined on the interval $(0,\infty)$ Tagliani [9] has shown that the distribution P_N always exists for $N\geq 4$. For $N=2$ the distribution only exists if $1<\mu_2/\mu_1^2<2$.

Recently Wang, Mead, and deLlano [7] applied the maximum-entropy approach to the extension of power series, specifically the equations of state for disks and spheres. They showed that one can convert the power-series problem into the moment problem. Given a function of x expressed as a series one can relate this to an integral over a distribution function as follows:

$$f(x)=1+\sum_{n=1}^{\infty} A_n x^n=\int_0^1 \frac{P(s)}{(1-xs)^{\alpha}} ds , \tag{4.4}$$

where α will usually be taken as an integer; the value of α will determine the asymptotic form of $f(x)$ as it approaches its radius of convergence. Expanding $(1-xs)^{-\alpha}$ about $(xs)=0$ using Newton's generalized binomial expansion one has

$$f(x)=\sum_{n=0}^{\infty} x^n \int_0^1 s^n \left[\frac{\alpha(\alpha+1)\cdots(\alpha+n-1)}{n!}\right] ds , \tag{4.5}$$

which gives the following relation between the coefficients A_n in the power-series expansion for $f(x)$ and the moments μ_n of $P(s)$:

$$\mu_n=\frac{n!}{\alpha(\alpha+1)\cdots(\alpha+n-1)} A_n . \tag{4.6}$$

Thus given the coefficients in the power series, we can calculate the moments for the distribution function $P(s)$. If we know $P(s)$, we can then calculate $f(x)$ by the integral in (4.4). It will turn out that $\alpha=1$ is the appropriate choice for our kinetic series and in that case we have

$$\alpha(\alpha+1)\cdots(\alpha+n-1)=n! \tag{4.7}$$

and hence

$$\mu_n=A_n , \tag{4.8}$$

so that the coefficients in the density series are the moments of $P(s)$. Knowledge of the A_n through A_N thus allows us to construct the maximum-entropy approximation P_N.

One cannot construct P_N for any set of $(N+1)$ μ's. These quantities must satisfy the Hausdorff criteria which are necessary and sufficient conditions for the μ's to be the moments of a non-negative function $P(x)$. For $P(x)$ on the interval (0,1), which is the interval used in (4.5), the Hausdorff conditions are

$$\sum_{m=0}^{k} (-1)^m \begin{bmatrix} k \\ m \end{bmatrix} \mu_{n+m}>0 , \qquad [\text{for } (n,k)=0 \text{ to } (n+k)\leq N] . \tag{4.9}$$

If $P(x)$ is given for a different interval, one must first rescale the moments to the interval (0,1).

Wang, Mead and deLlano [7] found that the virial series of (2.1) for the pressure of hard disks and spheres on converting the viral coefficients into moments using (4.6), only passed the Hausdorff test if they used $\alpha\geq 4$. Using the value of $\alpha=4$ they then found that the maximum-entropy method give an excellent fit to the molecular dynamics data for these hard particle systems, giving better accuracy than did Padée approximants.

It is interesting to note that for $\alpha=2$ the maximum-entropy method gives the exact equation of state for the one-dimensional fluid of hard rods with

$$P_N=1 \quad (\text{all } N) . \tag{4.10}$$

This is equivalent to

$$\lambda_n=0 \quad (\text{all } n, \text{ all } N) . \tag{4.11}$$

This is seen from (4.4) with $P(s)=1$ and $\alpha=2$

$$\int_0^1 \frac{P(s)}{(1-rs)^2} ds=\frac{1}{1-r}=\frac{\beta p}{\rho} , \tag{4.12}$$

where $r=\rho/\rho_m=\sigma\rho$.

Clearly the value of the exponent α in (4.5) is very important since, as this example shows, it determines the asymptotic form. The value of $\alpha=4$ used by Wang, Mead, and deLlano has no obvious physical meaning since it was chosen simply to make the moments pass the Hausdorff test. Unlike the case of the hard rod system, the disk and sphere systems each show a phase transition [12–14] at the respective relative densities $r^*=0.762$ and $r^*=0.613$. Thus the low density series cannot be used beyond this singular point and the singularity at close packing introduced by the maximum-entropy procedure has no physical significance.

For our kinetic equation we expect the following asymptotic form as $t\rightarrow\infty$. First we define

$$y=1-x , \tag{4.13}$$

which measures the distance from the final state, i.e., $y\rightarrow 0$ as $t\rightarrow\infty$. Since the final equilibrium state is not a special state (does not correspond to a phase transition density) then close to the large stage of the adsorption process we expect the simple form

$$\frac{dy}{dt}\sim-\frac{1}{\tau}y , \tag{4.14}$$

where τ is the characteristic relaxation time for the final stage of the dynamics. This gives

$$y\sim A \exp(-t/\tau) , \tag{4.15}$$

where A is a constant. Converting back to the variable x using (4.13) gives

$$t\sim-\tau\ln(1-x) , \tag{4.16}$$

and we expect our series to have the asymptotic form

$$t\sim\tau(x+\tfrac{1}{2}x^2+\tfrac{1}{3}x^3+\tfrac{1}{4}x^4+\cdots) . \tag{4.17}$$

We will compare the series we have obtained for rods and disks with this form shortly.

If we use the following form for our kinetic series

$$t/x=1+A_1x+A_2x^2+\cdots=f(x)=\int_0^1 \frac{P(s)}{(1-xs)} ds , \tag{4.18}$$

then as $x\rightarrow 1$ the integral will be dominated by $P(s)$ in the neighborhood of $s=1$ and we have the asymptotic form

$$t/x\sim P(1)\int_0^1 \frac{ds}{(1-xs)}=-\frac{1}{x}P(1)\ln(1-x) . \tag{4.19}$$

Comparing (4.16) we see that it has the correct asymptotic form with

$$\tau=P(1)\ . \tag{4.20}$$

We can also obtain an expression for the relaxation time in terms of the activity. We write our basic kinetic equation of (3.6) in the form

$$dx/dt=g(x)\ , \tag{4.21}$$

where $g(x)$ is defined by comparing (3.6) and (4.21). Then using the definition of y in (4.14) we have

$$dy/dt=-g\ . \tag{4.22}$$

The relaxation time is obtained by linearizing (4.22) about the final state, i.e., $y=0$

$$dy/dt\sim-\left[\frac{dg}{dy}\right]_{y=0} y\ . \tag{4.23}$$

We have then

$$\frac{1}{\tau}=\left[\frac{dg}{dy}\right]_{y=0}=\left[\frac{dg}{dx}\right]_{x=1}\frac{dx}{dy}=-\left[\frac{dg}{dx}\right]_{x=1}\ . \tag{4.24}$$

From (3.6) we see that the derivative of g requires knowledge of the derivative of $\ln\gamma$

$$\frac{\partial\ln\gamma}{\partial x}=\left[\frac{\partial\ln\gamma}{\partial r}\right]_{r^*}\frac{dr}{dx}=\left[\frac{\partial\ln\gamma}{\partial\ln r}\right]_{r^*}\ , \tag{4.25}$$

where we have used (3.3) to give $dr/dx=r^*$. Then finally

$$\frac{1}{\tau}=\frac{1}{\gamma^*}\left[1+\left[\frac{\partial\ln\gamma}{\partial\ln r}\right]_{r^*}\right]\ . \tag{4.26}$$

Using the form of $\ln\gamma(r)$ given in (2.8) we have the explicit form

$$\frac{1}{\tau}=\frac{1}{\gamma^*}\left[1+\sum_{n=1}^{\infty}(n+1)B_{n+1'}(b\rho_m)^n(r^*)^n\right]\ . \tag{4.27}$$

For the case of hard rods we have the closed form

$$\tau=(1-r^*)\exp[r^*/(1-r^*)]\ . \tag{4.28}$$

V. NUMERICAL EXAMPLES

The technical problem in the application of the maximum-entropy method is to calculate the parameters λ_0 through λ_N given the known moments μ_0 through μ_N. We sketch the method given by Mead and Papanicolaou [8]. We define the $(N\times N)$ matrix of second derivatives (Hessian)

$$\mathbf{H}=(H_{mn})\ , \tag{5.1}$$

where (for $m,n>0$)

$$H_{mn}=\frac{\partial^2\Gamma}{\partial\lambda_m\partial\lambda_n}=\langle x^{m+n}\rangle-\langle x^m\rangle\langle x^n\rangle\ , \tag{5.2}$$

where Γ is given in (4.3). The construction of this matrix requires the calculation of averages $\langle x^n\rangle$ through $n=2N$. We designate $\langle x^n\rangle$ as a quantity calculated using an estimate of $P_N(x)$ as opposed to the exact value μ_n. We then define the column vectors

$$\mathbf{m}=(\mu_n),\quad \boldsymbol{l}=(\lambda_n),\quad \mathbf{x}=(\langle x^n\rangle)\ , \tag{5.3}$$

where the index n runs from one to N. Starting with an initial guess for $\boldsymbol{l}$ (usually $\lambda_n=0$ for all n), an improved vector is given by

$$\boldsymbol{l}'=\boldsymbol{l}+\mathbf{H}^{-1}(\langle\mathbf{x}\rangle-\mathbf{m})\ . \tag{5.4}$$

All the quantities on the right-hand side of (5.4) are calculated using the previous estimate of the λ_n. One then iterates until there is agreement between $\boldsymbol{l}'$ and $\boldsymbol{l}$, say to ten figures. Typically this takes five to six iterations.

We begin with the series for t/x for rods given in (3.10) for the value of $r^*=\frac{1}{2}$ given in (2.19). If we take $\alpha=1$ in (4.4), which gives the form of (4.18), we have the case of (4.8) where the terms in the series for t/x are the moments of the distribution $P(x)$ without any alteration. The moments μ_0 through μ_7 are then given directly as the coefficients in (3.10); these moments satisfy the Hausdorff conditions of (4.9) so we can move on directly to the evaluation of the Γ_N (4.3), with $P_N=\exp(-\Gamma_N)$. For example, the first two maximum-entropy polynomials are found to be (for $r^*=\frac{1}{2}$)

$$\begin{aligned}\Gamma_1&=0.615\,746-1.126\,785x\ ,\\ \Gamma_2&=0.744\,059-1.783\,203x+0.609\,323x^2\ .\end{aligned} \tag{5.5}$$

The values of $P_N(x=1)$ are shown in Table I. From (4.20) we expect the quantities $P_N(1)$ to give estimates of the relaxation time. The exact value of this parameter is given by (4.28); for rods with $r^*=\frac{1}{2}$ we have

$$\tau=e/2=1.359\ . \tag{5.6}$$

We note that the numbers given in Table I do not represent a monotonic sequence of numbers that approach this value.

The functions $P_N(x)$ obtained from (5.5) are plotted in Fig. 4. We have grouped the functions as follows: (P_1,P_2), (P_3,P_4), (P_5,P_6), and (P_7). For this particular system these pairs seem to form a natural grouping. Notice that the functions oscillate more as N increases (this is required to give more moments exactly). Because of this oscillation, there is an erratic behavior of the end point $P_N(1)$ and hence the numbers in Table I do not show a uniform approach to the value of τ given in (5.6). The functions $P_N(x)$ are constructed to give a set of mo-

TABLE I. The values of $P_N(x=1)$ for rods and disks.

	$P_N(1)$	
N	Rods	Disks
1	1.6670	1.7239
2	1.5370	1.1359
3	1.1110	0.9519
4	1.2173	1.9876
5	1.6792	1.1783
6	1.5353	0.5785
7	0.8833	3.3345

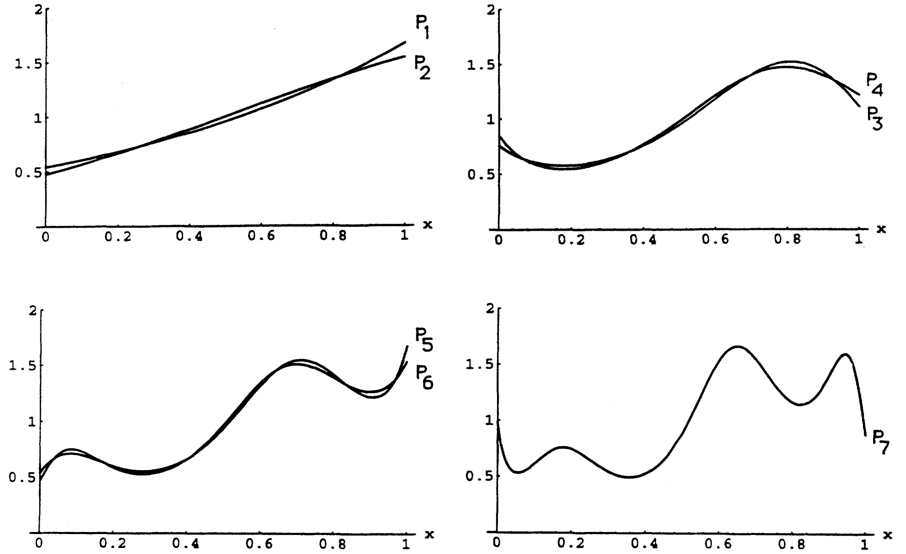


FIG. 4. The maximum-entropy distributions, $P_N(x)$, for $N=1$ to 7 for rods (with $r^*=\frac{1}{2}$) based on the $\Gamma_N(x)$ of (5.5). The endpoints $P_N(x=1)$ give an estimate of the asymptotic relaxation time and are listed in Table I.

ments exactly, but there is no requirement that the endpoint approach some prescribed number. While the functions $P_N(x)$ oscillate, the net result $t=t(x)$ does not; $t(x)$ is given by the integral in (4.18) which, even for $P_1(x)$, must be evaluated numerically.

We now compare the results obtained from the exact relation of (3.12) for rods with the $\Gamma_N(x)$ of (5.5) used in (4.18). Also, for comparison, we construct the following direct Padé approximants to the series of (3.10). We will designate a Padé approximate by the symbol $Q_{m,n}$ and refer to it as the $[m/n]$ approximant, where m and n are the total number of terms in the numerator and denominator, respectively. All of the Padé approximants have the following asymptotic form as $t \to \infty$

$$t \sim \left[\frac{1}{1-x/x_\sigma} \right] , \qquad (5.7)$$

i.e., a simple pole, the position of which is determined by the denominator root x_σ closest to the origin. We obtain $x_\sigma=1.689$ for the $[\frac{1}{2}]$ approximant and $x_\sigma=1.072$ and $x_\sigma=1.075$ for the $[\frac{4}{5}]$ and $[\frac{5}{4}]$ approximants. Thus as the number of exact coefficients that are used from (3.10) is increased, x_σ approaches one. Since the correct asymptotic form of $t(x)$ is given by (4.16), we see that the Padé approximants have the wrong asymptotic form and the wrong asymptote. All of the maximum-entropy approximations have the correct asymptotic form and the correct asymptote built in, even at the lowest level.

In Fig. 5 we compare the simplest maximum-entropy result, using $P_1(x)$, with the simplest Padé approximant, the $[\frac{1}{2}]$ approximant. Both of these results are constructed using only the coefficient of the linear term in (3.10). These curves are compared with the exact result of (3.12). The agreement of the simplest level of the maximum-entropy method with the exact result is quite impressive: this result has the correct functional form as $t \to \infty$ and has the correct asymptote (but not the correct value of τ as shown in Table I). By contrast the Padé approximant, constructed using the same input, has the wrong asymptote and the wrong functional form (one can clearly see the difference in the figure between the behavior of $[-\ln(1-x)]$ and $[1/(1-x/x_\sigma)]$.

If we were to plot the functions $t=t(x)$ obtained using P_1 through P_7 the results would be hard to distinguish in a figure. Instead we show some numerical comparisons in Table II between various of the P_N, the mean of the $[\frac{4}{5}]$ and $[\frac{5}{4}]$ Padé approximants (the data marked Padé-1) and of the exact result of (3.12). The two Padé approxi-

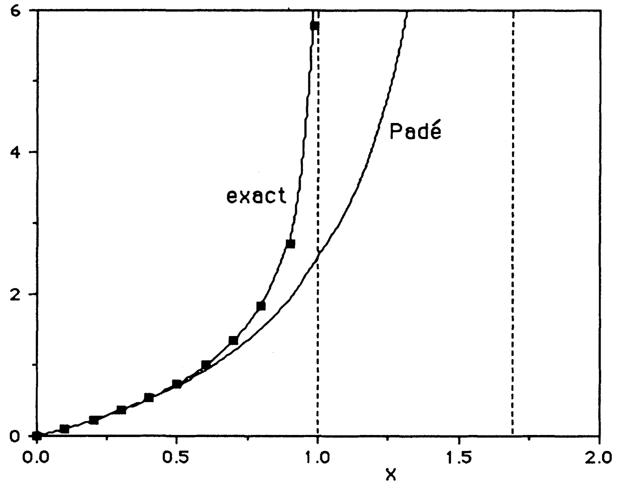


FIG. 5. Comparison of various versions of $t(x)$, the time required to give a given fraction of the final, equilibrium surface density for rods with $r^*=\frac{1}{2}$. The exact curve given by (3.12) is labeled as is the $[\frac{1}{2}]$ Padé approximant of (5.7). The solid points are the maximum-entropy result using $P_1(x)$; the points shown are for $x=0$ to 0.9 in steps of 0.1 and for $x=0.99$. The asymptote at $x=1$ is the position of the final equilibrium state; the $[\frac{1}{2}]$ Padé approximant has an incorrect asymptote at about $x=1.7$.

TABLE II. The values of $t(x)$ for various approximations for the adsorption of rods; all for $r^*=1/2$.

x	P_1	P_3	P_5	P_7	Padé-1	Padé-2	Exact
0.1	0.1064	0.1064	0.1064	0.1064	0.1064	0.1064	0.1064
0.3	0.3685	0.3683	0.3683	0.3683	0.3683	0.3683	0.3683
0.5	0.7381	0.7364	0.7365	0.7365	0.7365	0.7365	0.7365
0.7	1.3400	1.3290	1.3298	1.3297	1.3295	1.3297	1.3297
0.9	2.7888	2.6899	2.7112	2.7041	2.6853	2.7038	1.7065
0.99	6.2977	5.5313	5.9496	5.5922	4.7050	5.6805	5.7776
0.999	10.0694	8.1809	9.5905	7.9983	5.1343	8.5790	8.9010
1.0	∞	∞	∞	∞	5.1979	∞	∞

mants show close internal agreement; for example at $x=0.9$ one has $t=2.6874$ and $t=2.6833$ from the [$\frac{4}{5}$] and [$\frac{5}{4}$] approximants. The Padé approximants are finite at $x=1$ since the position of x_σ is greater than one ($x_\sigma=1.07$).

To see how well the asymptotic behavior of the adsorption process is given by (4.16) we can use the exact result of (3.12). We define $w=-\ln(1-x)$ and plot t/w obtained from (3.12) as a function of $1/w$. From (4.15) this should be a straight line with intercept and slope indicated below

$$t/w=\tau+\frac{1}{w}(\tau\ln A)\ . \tag{5.8}$$

Figure 6 shows this plot for $x=0.9$ to $x=1$. We see that over the last 10% of the relaxation process the asymptotic form of (4.16) holds quite closely. Since the values of τ obtained from $P_N(1)$, as illustrated in Table I, are quite bad, the maximum-entropy approximations will not give a good representation of the asymptotic behavior.

If we know that the asymptotic form of $t=t(x)$ is given by (4.16) then it is possible to construct a Padé approximant that has this form rather than using a direct Padé approximant to the series $t(x)$ that has the incorrect asymptotic form of (5.7). We take the series of (3.10) and divide this by the series for $[-\ln(1-x)]$ giving the new series

$$\begin{aligned}q(x)=t/[-\ln(1-x)]=1&+0.091\,97x+0.046\,252\,7x^2+0.026\,69x^3+0.016\,864\,9x^4\\&+0.011\,489x^5+0.008\,347\,33x^6+0.006\,395\,07x^7+\cdots\ .\end{aligned} \tag{5.9}$$

Now $t(x)$ is given by

$$t=-\ln(1-x)q(x)\ , \tag{5.10}$$

and this will be useful only if $q(x)$ has no singularities inside the unit circle. For both $Q_{4,5}$ and $Q_{5,4}$ the denominator root closest to the origin is at about $x_\sigma=1.151$ (specifically $x_\sigma=1.511$ and $x_\sigma=1.1513$, respectively). Thus $-\ln(1-x)$ determines the dominant form as $x\rightarrow 1$ with $q(x)$ acting as a modulating form that guarantees that the first eight terms in the expansion of $t(x)$ are exactly correct. At $x=1$ we have

$$\begin{aligned}Q_{4,5}(x=1)&=1.2430\ ,\\Q_{5,4}(x=1)&=1.2428\ .\end{aligned} \tag{5.11}$$

We note that

$$\tau=q(x=1)\ , \tag{5.12}$$

so $q(x)$ can be viewed as a series for the evaluation of τ. From the result $\tau=1.359$ of (5.6) we see that the Padé approximants miss the correct value, but give a better estimate than do the maximum-entropy results given in Table I. We show the mean value of the sum of $Q_{4,5}$ and $Q_{5,4}$ which is given as $t(x)$ in Table II (reported as Padé-

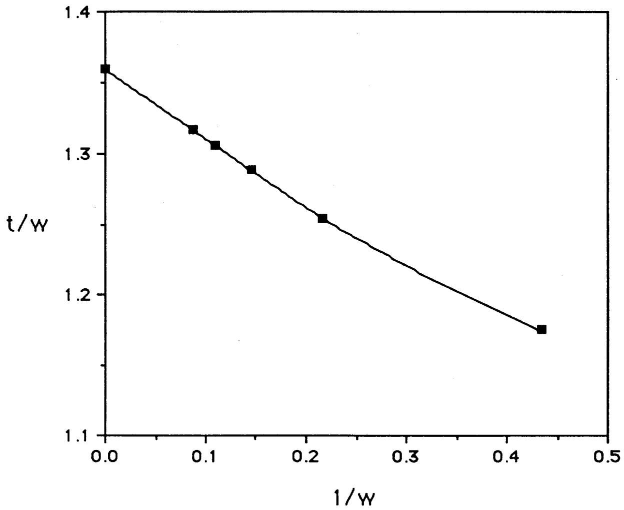


FIG. 6. A plot of t/w versus w [where $w=-\ln(1-x)$] as given by (3.12), the exact $t(x)$ for rods. The points shown cover the range $x=0.9$ to 1.0, the last 10% of the adsorption process. The linear form shows that the last stage of adsorption is simple exponential in the time and closely follows (5.11).

2). This Padé approximant result is in excellent agreement with the exact result and is as good as, or better, than the best maximum-entropy result.

We consider finally the series for τ given by (4.27). For rods $(b\rho_m)=1$ and $B_n'=1$ so we have

$$\frac{1}{\tau}=\frac{1}{\gamma^*}\sum_{n=0}^{\infty} n(r^*)^{n-1} . \tag{5.13}$$

Truncating the series at $n=7$ gives (using $r^*=\frac{1}{2}$ and $\gamma^*=e/2$ for our example)

$$\tau=1.388 , \tag{5.14}$$

which compares well with the exact value of $\tau=1.359$ of (5.6).

VI. DISKS

We will begin our discussion of the adsorption of disks where we left off in our discussion of the adsorption of rods in the previous section, namely with the relaxation time. Equation (4.27) gives the general formula for this quantity, involving γ^* and a series we will call $S(r)$

$$\frac{1}{\tau}=\frac{1}{\gamma^*}S(r) . \tag{6.1}$$

The quantity γ^* for disks is given by (2.18), with the Padé approximant given by (2.19) and (2.20). For disks the series $S(r)$ is given by

$$\begin{aligned} S(r)=1&+3.627\,599r+7.718\,075r^2+12.703\,65r^3\\ &+18.050\,78r^4+23.4196r^5+28.628\,51r^6\\ &+33.656\,01r^7+\cdots . \end{aligned} \tag{6.2}$$

The diagonal Padé approximant to $S(r)$ is

$$S(r)\approx Q_{4,4}=\left[\frac{1+38.448\,46r-22.786\,31r^2-0.950\,207\,5r^3}{1+38.134\,66r-34.923\,29r^2+3.386\,44r^3}\right] . \tag{6.3}$$

Using the Padé approximant of (6.3) with that of (2.20) for $\ln\gamma^*$ we obtain the data shown in Table III, giving γ^* and τ as a function of r^* up to $r^*=0.25$. The reason that we stop at $r^*=0.25$ for disks is that in order for our analysis to work we must have a very accurate value of γ^*.

Having reliable values of γ^* and τ for a range of r's up to $r^*=0.25$, we turn to the computation of the maximum-entropy polynomials from the series of (3.11). For $r^*=\frac{1}{4}$ the first two polynomials are

$$\begin{aligned} \Gamma_1&=0.665\,079-1.209\,670x ,\\ \Gamma_2&=1.369\,026-4.620\,020x+3.123\,566x^2 . \end{aligned} \tag{6.4}$$

The functions $P_N(x)$ are shown in Fig. 7. Unlike the case of rods, the pairs of function shown do not so closely resemble each other.

The values of the quantity

$$\tau=P_N(1) \tag{6.5}$$

as given in (4.20) are shown in Table I. From Table III we have the result that the correct value is $\tau=1.286$. As was the case for rods, we see that the values of τ given by (6.5) do not approach the correct value as N is increased. In Table IV we show the values of $t(x)$ computed from P_5 and P_7. We pick these two functions to illustrate since P_5 gives the best estimate of τ and P_7 gives the largest number of correct moments.

As a comparison we convert the series of (3.11) into the q series defined by

$$t=-\ln(1-x)q(x) , \tag{6.6}$$

with

$$\begin{aligned} q(x)=1&+0.098\,43x+0.382\,617x^2+0.017\,853\,2x^3\\ &+0.010\,122x^4+0.006\,742\,85x^5+0.004\,986\,8x^6\\ &+0.003\,923\,47x^7+\cdots . \end{aligned} \tag{6.7}$$

TABLE III. Equilibrium activity coefficient and relaxation time for disks.

r^*	γ^*	τ
0.0	1.0	1.0
0.5	1.2112	1.0073
1.0	1.5009	1.0318
1.5	1.9116	1.0788
2.0	2.5165	1.1572
2.5	3.4488	1.2816

TABLE IV. The values of $t(x)$ for various approximations for the adsorption of disks; all for $r^*=\frac{1}{4}$.

x	P_5	P_7	Mean Padé
0.1	0.1064	0.1064	0.1064
0.3	0.3686	0.3686	0.3686
0.5	0.7361	0.7361	0.7361
0.7	1.3229	1.3229	1.3229
0.9	2.6598	2.6646	2.6606
0.99	5.5519	6.1322	5.6683
0.999	8.3535	11.5748	8.7149
0.9999	11.0867	18.7760	11.613

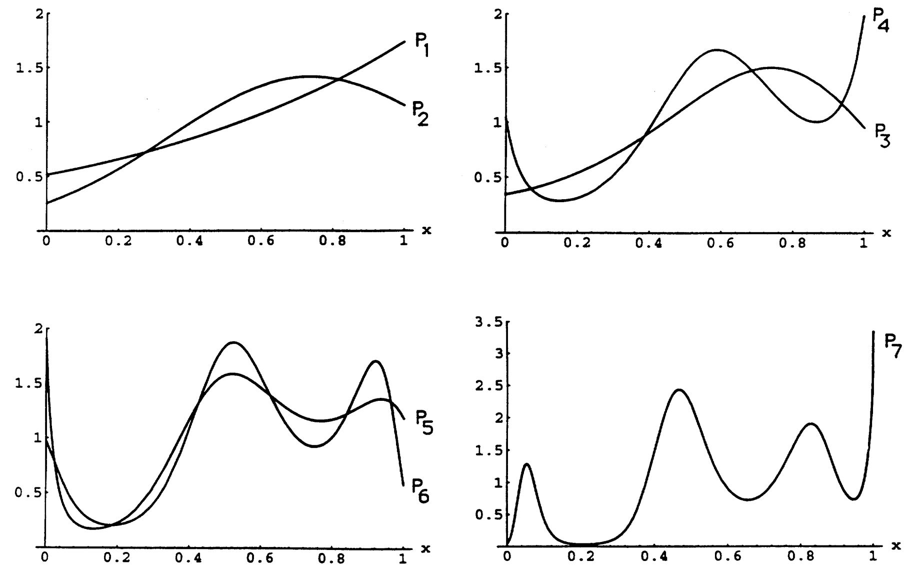


FIG. 7. The maximum-entropy distribution $P_N(x)$ for $N=1$ to 7 for disks (with $r^*=\frac{1}{4}$) based on the $\Gamma_N(x)$ of (6.4). The end points, $P_N(x=1)$, give an estimate of the asymptotic relaxation time and are listed in Table I.

The $Q_{4,5}$ and $Q_{5,4}$ approximants give very similar results. The closest denominator roots to the origin are, respectively, $x_\sigma = 1.017\,75$ and $x_\sigma = 1.020\,445$, so both approximants are finite at $x=1$. The values of $q(x=1)$ give the following estimates of τ: 1.269 69 and 1.263 618 both of which agree very well with the value given in Table III, namely, $\tau=1.286$. Numerical values of $t(x)$ as given by the mean of the q's given in (6.8) are listed in Table IV. The Padé approximants and P_5 agree very well with each other but they both disagree with the results of P_7 for $x>0.9$. Thus the more moments used does not necessarily give the better long time results. Figure 8 illustrates the use of the mean Padé approximant and P_5 giving x (fraction of final density) as a function of time.

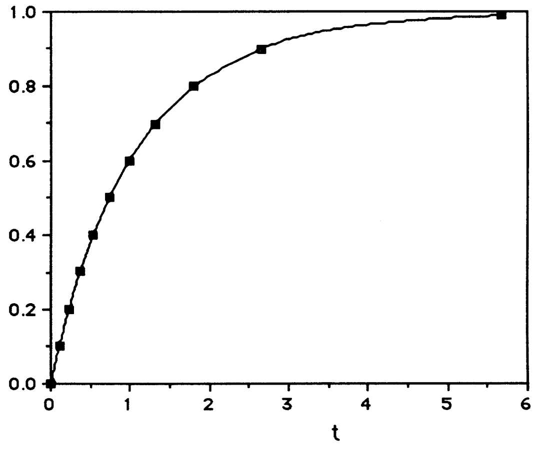


FIG. 8. The time dependence of the fraction of the equilibrium surface coverage for disks as a function of time (for $r^*=\frac{1}{4}$). The solid curve shown is for the mean result obtained with the two Padé approximants of (6.8) while the solid points are calculated using the maximum-entropy result obtained from $P_5(x)$; the data points shown are for $x=0$ to 0.9 in steps of 0.1 and for the point $x=0.99$.

VII. SUMMARY

We have illustrated how the equilibrium virial coefficients for hard disks can be used to describe the reversible adsorption kinetics of disks to a smooth, two-dimensional surface assuming instantaneous equilibrium on the surface. We have seen that the eight-term virial series can be converted into a seven-term series, Eq. (3.9), for the time as a function of the fraction of the equilibrium surface coverage. As is the case for the equilibrium virial series, this series for the time is well behaved with coefficients of uniform sign.

We then applied the maximum-entropy method to the extrapolation of the series, a procedure that has built in the correct asymptotic form and the correct asymptote. The disadvantage of this method is that the final result is obtained as a numerical integral. The marked oscillatory behavior of the $P_N(x)$ as shown in Figs. 4 and 7 is puzzling: we do not know whether $P_N(x)$ will approach a limiting form or whether the number of oscillations will increase indefinitely with N. Of course the function $t=t(x)$, through the integral of (4.18), does approach a limiting form (the exact kinetics) and this is a monotonically increasing function of x. The oscillations in the $P_N(x)$ seem to preclude these functions giving an accurate description of the very final stages of the adsorption process since the estimates $\tau=P_N(x=1)$ are erratic and do not seem to follow any trend as N is increased.

All in all, the maximum-entropy method and the Padé approximant method [using the form of (5.10)] seem to work about equally well, both methods being able to describe about 99% of the adsorption process as shown in Table IV. It is certainly useful to have an additional tool, the maximum-entropy method, available for the extension of series expansions.

[1] J. W. Evans, Rev. Mod. Phys. **65**, 1281 (1993).
[2] D. Poland, J. Stat. Phys. **61**, 765 (1990).
[3] D. Poland, Langmuir **7**, 514 (1991).
[4] D. Poland, Macromolecules **24**, 3352 (1991).
[5] D. Poland, Phys. Rev. A **44**, 7968 (1991).
[6] E. J. Janse van Rensburg, J. Phys. A **26**, 4805 (1993).
[7] D. Wang, L. R. Mead, and M. deLlano, J. Math. Phys. **32**, 2258 (1991).
[8] L. R. Mead and N. Papanicolaou, J. Math. Phys. **25**, 2404 (1984).
[9] A. Tagliani, J. Math. Phys. **34**, 326 (1993).
[10] K. F. Herzfeld and M. G. Mayer, J. Chem. Phys. **2**, 38 (1934).
[11] L. Tonks, Phys. Rev. **59**, 955 (1936).
[12] F. H. Ree and W. G. Hoover, J. Chem. Phys. **40**, 939 (1964).
[13] B. J. Alder and T. E. Wainwright, J. Chem. Phys. **33**, 1439 (1960).
[14] B.J. Alder and T. E. Wainwright, Phys. Rev. **127**, 359 (1962).