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Statistical Thermodynamic Treatment of Multilayer Adsorption–Migration Kinetics

Michael C. Fong*
Lockheed Martin Missiles and Space, Sunnyvale, California 94089

The transient multiple-layer (multilayer) adsorption and adsorption–migration phenomena are described with a statistical thermodynamic model. The key postulate for this model is that the transient process can be delineated by considering perturbation of the grand canonical ensemble characterizing either a multilayer adsorption or adsorption–migration system. Also, the derivative of the site partition function or adsorption site number (molecular coverage) for a given layer is affected only by the site distribution of its own layer and the two nearest-neighbor layers. With these postulates, differentiation of the grand partition function with time results in a system of first-order differential equations in terms of adsorption site numbers that describes the transient multilayer adsorption or adsorption–migration process. Its solution determines the time-varying layer-by-layer deposit buildup on a smooth surface under constant molecular impingement. In either the adsorption or adsorption–migration case, the statistical thermodynamic solution has been proven to be equivalent to that based on the classical kinetic theory, which has been verified by laboratory test data.

Nomenclature

A_i = adsorption coefficient; Eq. (41)
a_i = $x_i - x_{i+1}$ site available for the ith layer
D_i = desorption coefficient; Eq. (45)
E_i = ith layer desorption energy
E_{mi} = energy of migration; Eq. (47)
F_i = normalized migration function [Eq. (42)], $(f_{i-1} - f_i)/x_0$
F^* = migration function; Eq. (46)
$f_i(\eta)$ = migration function; Eq. (38)
h = Planck constant
I_j = moment of inertia of the jth rotational degree of freedom
k = Boltzmann constant
L^n = configuration quantity: line, area, or volume for $n = 1, 2$, or 3; Eq. (27)
M_{ij} = migration coefficient; Eq. (47)
m = maximum number of adsorbed layers at time t
N_i = number of molecules or atoms in ith layer
$\dot{n}$ = incident molecular number flux (number per second)
P = pressure
Q_s = grand partition function
q_i = partition function for the ith adsorption layer
q_{rt} = rotational partition function
q_{tr} = translational partition function
q_{vb} = vibrational partition function
R = universal gas constant
S_i = ith layer sticking coefficient
S_i^* = ith layer sticking coefficient; Eq. (36)
T = temperature
t = time
U_i = potential of adsorption
V = volume
x_i = number of adsorbed molecules in the ith layer
x_0 = total number of bare surface sites
x_i^0 = number of adsorbed molecules under equilibrium condition; Eqs. (5) and (38)
y_i = number of migrating molecules in the ith layer
y_i^0 = number of adsorbed molecules under equilibrium condition; Eq. (38)
α_{ij} = partition function term; Eq. (11)
β_{ij} = migration constant; Eq. (47)
$\Delta\eta_i$ = migration perturbation variable
$\Delta\xi_i$ = adsorption perturbation variable
η_i = site element in the ith layer (referring to y_i)
θ_i = surface coverage parameter, $(x_i - x_{i+1})/x_0$ or $[(x_{i-1} - x_i) + (y_{i-1} - y_i)]/x_0$
$\dot{\theta}_j$ = derivative of θ_i with time
λ_i = total activity for ith layer, μ_i/kT
μ_i = chemical potential
μ_i^0 = unit pressure chemical potential; Eq. (30)
ξ_i = site element in the ith layer (referring to x_i)
σ = symmetry number; Eq. (28)
σ_0 = number of molecules in a monolayer; Eq. (25)
τ_a = lattice fluctuation time $\approx 10^{-13}$ s
τ_i = residence time of adsorbed molecules in the ith layer, $\tau_a \exp(E_i/kT)$, $i = 0, 1, 2, \ldots$
τ_i^* = ith layer residence time; Eq. (36)

Introduction

BOTH the equilibrium single-layer (Langmuir) and multilayer [Brunauer, Emmett, and Teller (BET)] adsorption problems have been treated extensively with the statistical thermodynamic approach by various authors.[1–3] However, much less attention has been accorded their transient counterparts, that is, the adsorption kinetic process (or time-dependent deposit accretion) from the initial bare-surface state to the equilibrium state. In this paper, we present a transient statistical thermodynamic solution of adsorption kinetics by assuming that the adsorption process remains in a quasi-equilibrium state but allows small perturbation of thermodynamic quantities. This perturbation approach is applicable not only to the single-layer or multilayer adsorption kinetic process, each of which involves a constant incident molecular flux, but also to the combined adsorption and interlayer migration processes. The objective of this paper is to prove the validity of this relaxation scheme, in that the time-varying statistical thermodynamic solution is equivalent to the solution based on the classical kinetic theory, which has been compared satisfactorily with laboratory test data.[4,5]

In accordance with the statistical thermodynamic theory, a generalized adsorption–migration system can be described by a grand canonical ensemble comprising the thermodynamics variables V, T, and $\mu_1, \mu_2, \mu_3, \ldots$, with $N_1, N_2, N_3, \ldots$ fluctuating about their

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*Technical Consultant, Materials and Processes Engineering; currently Retired, 301 Sunkist Lane, Los Altos, CA 94022. Associate Fellow AIAA.

mean values. Our approach to the transient adsorption–migration problem is 1) to utilize a perturbation adsorption variable for each layer to ascertain the time-varying properties of the grand canonical ensemble and 2) to differentiate the grand partition function with time from which a system of differential equations describing the adsorption or adsorption–migration kinetics can be obtained. The solutions to these differential equations describe the transient adsorption or adsorption–migration process based on the statistical thermodynamic theory.

In the ensuing sections, the basic scheme for our transient statistical thermodynamics model is first discussed, followed by a description of the solutions for multilayer adsorption and adsorption–migration kinetics. The well-proven kinetic theory results discussed in Refs. 4 and 5 are used to establish the validity of the transient statistical thermodynamic model.

Transient Statistical Thermodynamics Model

The grand partition function for a generalized adsorption kinetics system (grand canonical ensemble) can be expressed as follows:

$$Q_s(x_i, x_0, T) = \sum_{a_i=0}^{a_m} \frac{x_0!\, q_1^{a_1}(q_1 q_2)^{a_2}\cdots\left(\prod_{i=1}^{m} q_i\right)^{a_m}}{a_0!\, a_1!\cdots a_m!} \tag{1}$$

where

$$a_i = x_i - x_{i+1} \tag{2}$$

represents the net sites available for the ith layer and where x_i is the number of adsorbed molecules in the ith layer. In anticipation of using $\ln Q_s$, we made use of the maximum-term approximation method in statistical thermodynamics, in that the logarithm of a sum can be approximated by the maximum term in the sum. Hence, the probability for the maximum term can be expressed as follows:

$$Q_s(x_i, x_0, T) = \frac{x_0!\, q_1^{x_1} q_2^{x_2}\cdots q_i^{x_i}\cdots q_m^{x_m}}{(x_0 - x_1)!(x_1 - x_2)!\cdots(x_{m-1} - x_m)!\, x_m!} \tag{3}$$

where x_m represents the adsorption site number of the uppermost adsorption layer. It is seen that Eq. (1) or (3) is in a generalized form without explicitly expressing the time-dependent features. The fraction on the right-hand side of Eq. (1) or (3) indicates the number of degenerate eigenstates or the number of adsorbed molecules distributed over available sites in each layer. Also, the adsorbed molecules are treated as spherical pseudoatoms that undergo interlayer molecular bombardments and exchanges.

To formulate a transient adsorption theory, we postulate that the adsorption site distribution over each layer is characterized by its average site number (or coverage value) without considering detailed interactions within the layer. As discussed in Refs. 4 and 5, the average site number of the ith layer, along with its derivative, under dynamic equilibrium conditions, is affected only by its nearest-neighbor layers. This nearest-neighbor relationship is shown metaphorically in Figs. 1 and 2 where the particles (or sites) belonging to the ith layer directly cover only the $(i-1)$th layer and the ith layer is directly covered only by the particles belonging to the $(i+1)$th layer. For the more general adsorption–migration problem, interlayer migration (molecular hopping) to and from other layers is added to the adsorption–desorption mode.

Adsorption Kinetics

To consider the adsorption–desorption kinetic problem first, the ith-layer average site number x_i can be expressed in terms of the nearest-neighbor site quantities as follows:

$$x_i = x_i(\xi_{i-1}, \xi_i, \xi_{i+1}) \tag{4}$$

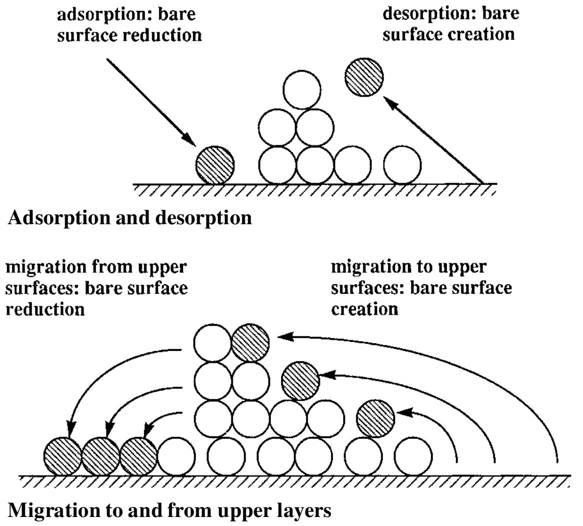

Fig. 1 Sketches showing bare-surface molecular adsorption and migration.

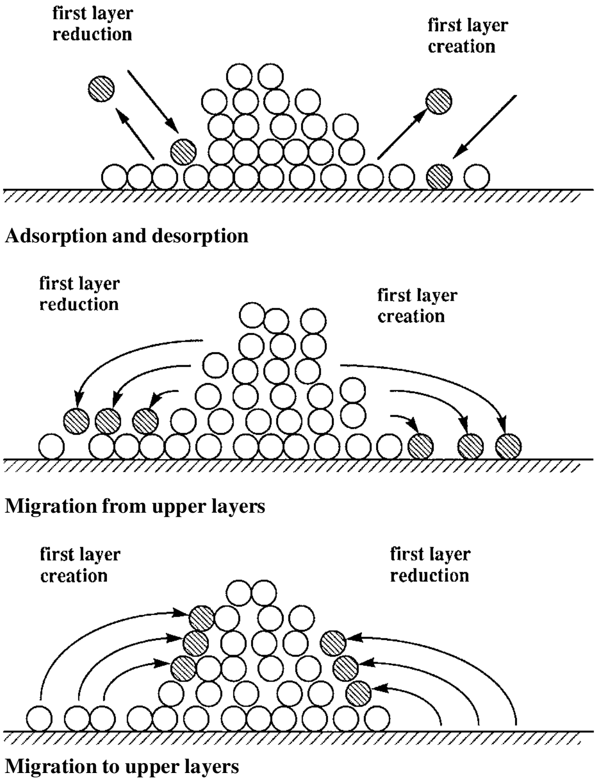

Fig. 2 Sketches showing upper-surface molecular adsorption and migration.

where ξ_{i-1}, ξ_i, and ξ_{i+1} represent the site element terms of the ith and neighboring layers. To ascertain the time-varying behavior of the grand canonical ensemble (denoted by the grand partition function), we introduce a perturbation variable for adsorption as follows:

$$x_i = x_i^0 + \Delta\xi_i \tag{5}$$

where x_i^0 is the number of adsorbed molecules under equilibrium conditions, x_i is the time-dependent number of adsorbed molecules, and $\Delta\xi_i$ is the perturbation variable. Note that under equilibrium or steady-state conditions, x_i is the same as x_i^0 in Eq. (3). Substitution of Eq. (5) into Eq. (3) results in

$$Q_s = \frac{x_0!\prod_{i=1}^{m} q_i^{(x_i - \Delta\xi_i)}}{\prod_{i=0}^{m}[(x_i - \Delta\xi_i) - (x_{i+1} - \Delta\xi_{i+1})]!} \tag{6}$$

With the aid of Stirling's approximation for factorials

$$\ln N! = N \ln N - N \tag{7}$$

and the chemical potential relation

$$-\left(\frac{\partial \ln Q_s}{\partial x_i}\right)_{x_0,T} = \frac{\mu_i}{kT}, \qquad i = 1, 2, \ldots \tag{8}$$

where μ_i is the maximum chemical potential for the ith layer, layer-by-layer differentiation of $\ln Q_s$ with respect to x_i produces the following system of equations[4]:

$$\begin{aligned} &\lambda_i q_i(\Delta\xi_{i-1} - \Delta\xi_i) - (\Delta\xi_i - \Delta\xi_{i+1}) \\ &\quad = \lambda_i q_i(x_{i-1} - x_i) - (x_i - x_{i+1}), \qquad i = 1, 2, \ldots, m \end{aligned} \tag{9}$$

where both x_0 (for $i = 1$) and $\lambda_i = \exp(\mu_i/kT)$, which is total activity, are independent of time. Note that derivation of Eq. (9) includes the assumption $\partial\Delta\xi_i/\partial x_i \ll 1$. The left-hand side of Eq. (9) can be expressed in a matrix form as follows:

$$\begin{bmatrix} \lambda_1 q_1 & -(1+\lambda_1 q_1) & 1 & 0 & & & \cdots & 0 \\ 0 & \lambda_2 q_2 & -(1+\lambda_2 q_2) & 1 & 0 & & \cdots & 0 \\ 0 & 0 & \lambda_3 q_3 & -(1+\lambda_3 q_3) & 1 & 0 & \cdots & 0 \\ 0 & 0 & 0 & \cdots & & & & \\ & \vdots & & & \vdots & & & \\ 0 & \cdots & \cdots & 0 & \lambda_{m-1} q_{m-1} & & & -(1+\lambda_{m-1} q_{m-1}) \\ 0 & \cdots & \cdots & 0 & 0 & & & \lambda_m q_m \end{bmatrix} \begin{bmatrix} \Delta\xi_0 \\ \Delta\xi_1 \\ \Delta\xi_2 \\ \vdots \\ \Delta\xi_{m-2} \\ \Delta\xi_{m-1} \end{bmatrix} \tag{10}$$

or

$$\begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} & \cdots & \alpha_{1m} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} & \cdots & \alpha_{2m} \\ \vdots & & & & \vdots \\ \alpha_{m1} & \alpha_{m2} & \alpha_{m3} & \cdots & \alpha_{mm} \end{bmatrix} \begin{bmatrix} \Delta\xi_0 \\ \Delta\xi_1 \\ \vdots \\ \Delta\xi_{m-1} \end{bmatrix} \tag{11}$$

where

$$\begin{gathered} \alpha_{ii} = \lambda_i q_i, \qquad \alpha_{i,i+1} = -(1+\lambda_i q_i), \qquad \alpha_{i,i+2} = 1 \\ \alpha_{i,i-h} = 0, \qquad i > h \geq 1 \\ \alpha_{i,i+k} = 0, \qquad k \geq 3 \\ \Delta\xi_m = 0 \end{gathered} \tag{12}$$

Thus, each row on the left-hand side of Eq. (9) has no more than three terms as shown here:

$$\begin{gathered} \alpha_{11}\Delta\xi_0 + \alpha_{12}\Delta\xi_1 + \alpha_{13}\Delta\xi_2 \\ \alpha_{22}\Delta\xi_1 + \alpha_{23}\Delta\xi_2 + \alpha_{24}\Delta\xi_3 \\ \vdots \\ \alpha_{i,i}\Delta\xi_{i-1} + \alpha_{i,i+1}\Delta\xi_i + \alpha_{i,i+2}\Delta\xi_{i+1} \\ \vdots \\ \alpha_{m-1,m-1}\Delta\xi_{m-2} + \alpha_{m-1,m}\Delta\xi_{m-1} \\ \alpha_{m,m}\Delta\xi_{m-1} \end{gathered} \tag{13}$$

Based on the postulate that the distribution of adsorbed particles over the ith layer is dependent only on the properties of its immediate neighboring layers (upper and lower), the total differential of x_i can be written as

$$dx_i = \frac{\partial x_i}{\partial \xi_{i-1}} d\xi_{i-1} + \frac{\partial x_i}{\partial \xi_i} d\xi_i + \frac{\partial x_i}{\partial \xi_{i+1}} d\xi_{i+1} \tag{14}$$

As discussed in Ref. 4, the right-hand side of Eq. (14) is the same as Eq. (13), where $\Delta\xi_i$ is conceptually the same as the differential $d\xi_i$. With this argument, the derivative of x_i with respect to time t over the residence time τ_i for each layer can be expressed as

$$\begin{aligned} \frac{dx_1}{dt}\tau_0 &= \alpha_{11}\Delta\xi_0 + \alpha_{12}\Delta\xi_1 + \alpha_{13}\Delta\xi_2 \\ \frac{dx_2}{dt}\tau_1 &= \alpha_{22}\Delta\xi_1 + \alpha_{23}\Delta\xi_2 + \alpha_{24}\Delta\xi_3 \\ \frac{dx_3}{dt}\tau_2 &= \alpha_{33}\Delta\xi_2 + \alpha_{34}\Delta\xi_3 + \alpha_{35}\Delta\xi_4 \\ &\vdots \\ \frac{dx_i}{dt}\tau_{i-1} &= \alpha_{i,i}\Delta\xi_{i-1} + \alpha_{i,i+1}\Delta\xi_i + \alpha_{i,i+2}\Delta\xi_{i+1} \\ &\vdots \\ \frac{dx_{m-1}}{dt}\tau_{m-2} &= \alpha_{m-1,m-1}\Delta\xi_{m-2} + \alpha_{m-1,m}\Delta\xi_{m-1} \\ \frac{dx_m}{dt}\tau_{m-1} &= \alpha_{m,m}\Delta\xi_{m-1} \end{aligned} \tag{15}$$

where τ_i is defined as

$$\tau_i = \tau_a \exp(E_i/RT) \tag{16}$$

Furthermore, the partial derivatives $\partial x_i/\partial\xi_i$ can be correlated with the partition function terms $\lambda_i q_i$ from Eqs. (10–14), yielding the following:

$$\begin{gathered} \frac{\partial x_i}{\partial \xi_{i-1}} = \alpha_{i,i} = \lambda_i q_i, \qquad \frac{\partial x_i}{\partial \xi_i} = \alpha_{i,i+1} = -(1+\lambda_i q_i) \\ \frac{\partial x_i}{\partial \xi_{i+1}} = \alpha_{i,i+2} = 1 \end{gathered} \tag{17}$$

We can then express Eq. (15) as follows:

$$\begin{aligned} \frac{dx_1}{dt}\tau_0 &= \lambda_1 q_1\Delta\xi_0 - (1+\lambda_1 q_1)\Delta\xi_1 + \Delta\xi_2 \\ \frac{dx_2}{dt}\tau_1 &= \lambda_2 q_2\Delta\xi_1 - (1+\lambda_2 q_2)\Delta\xi_2 + \Delta\xi_3 \\ &\vdots \qquad\qquad \vdots \\ \frac{dx_i}{dt}\tau_{i-1} &= \lambda_i q_i\Delta\xi_{i-1} - (1+\lambda_i q_i)\Delta\xi_i + \Delta\xi_{i+1} \\ &\vdots \qquad\qquad \vdots \\ \frac{dx_{m-1}}{dt}\tau_{m-2} &= \lambda_{m-1} q_{m-1}\Delta\xi_{m-2} - (1+\lambda_{m-1} q_{m-1})\Delta\xi_{m-1} \\ \frac{dx_m}{dt}\tau_{m-1} &= \lambda_m q_m\Delta\xi_{m-1} \end{aligned} \tag{18}$$

Finally, the system of generalized immobile transient multilayer adsorption differential equations, Eq. (9), can be written in the matrix form as follows:

$$\tau_{i-1}\frac{dx_i}{dt} = \lambda_i q_i(x_{i-1} - x_i) - (x_i - x_{i+1}) \tag{19}$$

where $i = 0, 1, 2, \ldots, m$, and $x_{m+1} = 0$, because there are only m layers. By expressing x_i in terms of a site coverage variable θ_i, we have

$$\theta_i = (x_{i-1} - x_i)/x_0, \qquad i = 1, 2, \ldots \tag{20}$$

where the zeroth-order layer x_0 indicates the bare surface coverage, that is, the maximum number of available sites of a bare surface. The derivatives $\mathrm{d}x_i/\mathrm{d}t$ can be written as

$$\begin{aligned}
\frac{\mathrm{d}x_1}{\mathrm{d}t} &= -\dot{\theta}_0 \\
\frac{\mathrm{d}x_2}{\mathrm{d}t} &= -(\dot{\theta}_0 + \dot{\theta}_1) \\
\frac{\mathrm{d}x_3}{\mathrm{d}t} &= -(\dot{\theta}_0 + \dot{\theta}_1 + \dot{\theta}_2) \\
&\vdots \\
\frac{\mathrm{d}x_i}{\mathrm{d}t} &= -\sum_{j=0}^{i-1} \dot{\theta}_j
\end{aligned} \tag{21}$$

where the negative sign indicates site reduction. It follows that Eq. (19) can be written as

$$\begin{aligned}
-\dot{\theta}_0 \tau_0 &= \lambda_1 q_1 \theta_0 - \theta_1 \\
-(\dot{\theta}_0 + \dot{\theta}_1)\tau_1 &= \lambda_2 q_2 \theta_1 - \theta_2 \\
-(\dot{\theta}_0 + \dot{\theta}_1 + \dot{\theta}_2)\tau_2 &= \lambda_3 q_3 \theta_2 - \theta_3 \\
\vdots \qquad & \qquad \vdots \\
-\left(\sum_{j=0}^{i-1} \dot{\theta}_j\right)\tau_{i-1} &= \lambda_i q_i \theta_{i-1} - \theta_i \\
\vdots \qquad & \qquad \vdots
\end{aligned} \tag{22}$$

and the corresponding matrix equation of Eq. (22) can be expressed as follows:

$$-\left(\sum_{j=0}^{i-1} \dot{\theta}_j\right)\tau_{i-1} = \lambda_i q_i \theta_{i-1} - \theta_i, \qquad i = 1, 2, \ldots \tag{23}$$

In Ref. 1, the adsorption matrix equation derived based on the classical kinetic theory is of the form

$$-\left(\sum_{j=0}^{i-1} \dot{\theta}_j\right) = \frac{\dot{n} S_{i-1}}{\sigma_0}\theta_{i-1} - \frac{\theta_i}{\tau_a}\exp\left(-\frac{E_{i-1}}{RT}\right) \qquad i = 1, 2, \ldots \tag{24}$$

where $\dot{n}$ is the incident number flux (number per second) onto all layers, S_{i-1} is the sticking coefficient for the $(i-1)$th layer, σ_0 is the number of molecules for a monolayer (or total coverage or sites, the same as x_0), and the exponential product term is defined by the residence time expression in Eq. (16). It is seen that for Eqs. (23) and (24) to be equal (that is, the statistical thermodynamic and kinetic theory results being the same), the following expression must be true:

$$\lambda_i q_i = \dot{n}\tau_{i-1} S_{i-1}/\sigma_0 \tag{25}$$

To prove this equivalence, we should first point out that in our multilayer adsorption scheme, we consider a time-dependent BET-type adsorption of incident molecules, where a sticking coefficient or accommodation coefficient for each layer is used to indicate the molecular interaction properties. Hence, we start out by determining the statistical thermodynamic properties of the incident molecules for each layer and then establish correlation with the kinetic theory results, that is, Eq. (25). As in the classical statistical thermodynamic theory, a harmonic oscillator model is utilized to describe the generalized polyatomic (including atomic) multilayer adsorption characteristics. The present harmonic oscillator model involves translational, rotational, and vibrational partition functions with n degrees of freedom, where $n = 1$, 2, or 3 (the electronic partition function is not included here). Note that some of these modes may not be present for particular cases, such as the absence of the rotational partition function for the monatomic case with $n = 1$. The total partition function q_i for gaseous molecules active in the ith layer can be written as

$$q_i = q_{\mathrm{tr}} q_{\mathrm{rt}} q_{\mathrm{vb}} \exp(U_{i-1}/RT) \tag{26}$$

where U_{i-1} is potential of adsorption for the $(i-1)$th layer where adsoprtion occurs, and the specific partition function expressions are as follows.

The translational function expression is

$$q_{\mathrm{tr}} = (2\pi mkT/h^2)^{n/2} L^n \tag{27}$$

the rotational function expression is

$$q_{\mathrm{rt}} = \frac{1}{\sigma\pi}\left[8\pi^3\left(\prod_{j=1}^{n} I_j\right)^{1/n} kT \Big/ h^2\right]^{n/2} \tag{28}$$

and the vibrational expression is

$$q_{\mathrm{vb}} = \prod_{j=1}^{n} \frac{\exp(-hv_j/2kT)}{1 - \exp(-hv_j/2kT)} \tag{29}$$

where σ is the symmetry number used to correct for repeated counting of indistinguishable configurations in the classical phase integral.[1]

To derive an appropriate statistical thermodynamic expression for the chemical potential parameter λ_i, we need to first examine the chemical potential term μ_i, which can be written as follows:

$$\mu_i/kT = \mu_i^0\big/kT + \ln P \tag{30}$$

where μ_i^0 is the standard chemical potential of a molecule at unit pressure with n degrees of freedom and can be expressed as

$$\begin{aligned}
\mu_i^0\big/kT &= -\ln(q_{\mathrm{tr}} q_{\mathrm{rt}} q_{\mathrm{vb}}/N_i) \\
&= -\ln\left[(2\pi mkT/h^2)^{\frac{3}{2}}(L^n/N_i)(q_{\mathrm{rt}} q_{\mathrm{vb}})\right]
\end{aligned} \tag{31}$$

where N_i is number of molecules or atoms in the ith layer. As indicated in Refs. 1 and 2, the bracketed quantity in Eq. (31) must have the dimension of pressure, which is why the unit pressure term is used here (note that for notational simplicity, subscript i is not used for the partition functions).

To demonstrate the correlation, we consider a general case with $n = 3$, where L^n indicates a volume. It follows that

$$L^n\big/N_i = kT \tag{32}$$

Then, Eq. (31) becomes

$$\mu_i^0\big/kT = -\ln\left[(2\pi mkT/h^2)^{\frac{3}{2}} kT(q_{\mathrm{rt}} q_{\mathrm{vb}})\right] \tag{33}$$

Substituting the expressions in Eqs. (28), (29), and (33) into the following λ_i equation

$$\lambda_i = \exp(\mu_i/kT) = \exp\left[\left(\mu_i^0\big/kT\right) + \ln P\right] \tag{34}$$

we obtain the following expression (for $n = 3$):

$$\begin{aligned}
\lambda_i &= P\exp\left\{-\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} kT(q_{\mathrm{rt}} q_{\mathrm{vb}})\right]\right\} \\
&= P\left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} kT(q_{\mathrm{rt}} q_{\mathrm{vb}})\right]^{-1} = P\left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} kT\right]^{-1} \\
&\quad \times \left\{\frac{1}{\sigma\pi}\left[\frac{8\pi^3(I_1 I_2 I_3)^{\frac{1}{3}} kT}{h^2}\right]^{\frac{3}{2}}\right\}^{-1}\left[\prod_{j=1}^{3}\frac{\exp(-hv_j/2kT)}{1 - \exp(-hv_j/2kT)}\right]^{-1}
\end{aligned} \tag{35}$$

Furthermore, by combining Eqs. (26), (30), and (34), the $\lambda_i q_i$ product for the ith layer can be expressed as follows:

$$\begin{aligned}\lambda_i q_i &= \exp\left[\left(\frac{\mu^0}{kT}\right) + \ell n\, P\right]\left[q_{\mathrm{tr}} q_{\mathrm{rt}} q_{\mathrm{vb}} \exp\left(\frac{U_{i-1}}{RT}\right)\right] \\ &= \exp[-\ell n(q_{\mathrm{tr}} q_{\mathrm{rt}} q_{\mathrm{vb}}/N_i) + \ell n\, P]\left[q_{\mathrm{tr}} q_{\mathrm{rt}} q_{\mathrm{vb}} \exp\left(\frac{U_{i-1}}{RT}\right)\right] \\ &= \left[\frac{P}{q_{\mathrm{tr}} q_{\mathrm{rt}} q_{\mathrm{vb}}/N_i}\right]\left[q_{\mathrm{tr}} q_{\mathrm{rt}} q_{\mathrm{vb}} \exp\left(\frac{U_{i-1}}{RT}\right)\right] \\ &= \frac{P}{kT}\exp\left(\frac{U_{i-1}}{RT}\right) = \frac{N_i}{\sigma_0}\exp\left(\frac{U_{i-1}}{RT}\right) \\ &= \frac{\dot{n} S^*_{i-1}}{\sigma_0}\left[\tau^*_{i-1}\exp\left(\frac{U_{i-1}}{RT}\right)\right] \\ &= \frac{\dot{n} S_{i-1}}{\sigma_0}\left[\tau_a \exp\left(\frac{E_{i-1}}{RT}\right)\right] = \frac{\dot{n}\tau_{i-1} S_{i-1}}{\sigma_0}\end{aligned} \tag{36}$$

In this derivation, we have introduced two tentative adsorption quantities S^*_{i-1} (sticking coefficient) and τ^*_{i-1} (residence time), as well as the incident flux $\dot{n}$, to characterize N_i. By using proper correction factors where needed and noting that U_{i-1} differs from E_{i-1} only by an $h\nu$ factor,[1,3] it can be established that S^*_{i-1} and τ^*_{i-1} are equivalent to τ_a and S_{i-1}. It follows from this derivation that Eqs. (23) and (24) are identical.

To recapitulate, we have demonstrated that on the basis of the harmonic oscillator model in statistical thermodynamics, the $\lambda_i q_i$ quantity can be expressed in terms of macroscopic thermodynamic functions used in the kinetic theory approach. As in the equilibrium case,[2,3] the transient BET solution based on the statistical thermodynamic theory is identical to that based on the kinetic theory.[4,5]

Adsorption–Migration Kinetics

In this case, we postulate that the grand canonical ensemble comprises two different types of uncoupled adsorbates, one characterized by adsorption–desorption under constant molecular impingement and the other characterized by interlayer migration (molecular hopping to and from other layers). The grand partition function involving these two types of molecules can be expressed as

$$Q_n = \frac{x_0!\prod_{i=1}^{n}\left(q_{x_i}^{x_i} q_{y_i}^{y_i}\right)}{x_m!\,y_m!\prod_{i=1}^{n}[(x_{i-1} - x_i) + (y_{i-1} - y_i)]!} \tag{37}$$

Similar to the adsorption-only problem, Eq. (37) can be considered to be under equilibrium conditions, where x_i and y_i may be written as x_i^0 and y_i^0. By introducing perturbation variables $\Delta\xi_i$ and $\Delta\eta_i$ in the site quantities as follows:

$$x_i^0 = x_i - \Delta\xi_i, \qquad y_i^0 = y_i - \Delta\eta_i - f_i(\eta) \tag{38}$$

the grand partition function, Eq. (37), then becomes

$$\begin{aligned}Q_n = {}&\left\{x_0!\prod_{i=1}^{n} q_{x_i}^{(x_i - \Delta\xi_i)} q_{y_i}^{[y_i - \Delta\eta_i - f_i(\eta)]}\right\}\Big/(x_n - \Delta\xi_n)! \\ &\times [y_n - \Delta\eta_n - f_n(\eta)]!\prod_{i=1}^{n}([|x_{i-1} - \Delta\xi_{i-1}| - (x_i - \Delta\xi_i)] \\ &+ \{(y_{i-1} - \Delta\eta_{i-1} - f_{i-1}|\eta) - [y_i - \Delta\eta_i - f_i(\eta)]\})!\end{aligned} \tag{39}$$

Note that the migration function $f_i(\eta)$ is introduced to account for the nonlinear effects of the site product terms that are present for migration problems.[5] Layer-by-layer differentiation of Eq. (39) then yields a system of quasi-linear differential equations as follows:

$$\begin{aligned}-\left(\sum_{j=0}^{i-1}\dot{\theta}_j\right)\tau_{i-1} = {}&[\lambda_i q_i \theta_{i-1} - \theta_i] \\ &- [F_{i-1}(\theta_{i-1}, f_{i-1}) - F_i(\theta_i, f_i)], \qquad i = 1, 2, \ldots\end{aligned} \tag{40}$$

where the site-coverage variable θ_i, now defined as

$$\theta_i = [(x_{i-1} - x_i) + (y_{i-1} - y_i)]/x_0, \qquad i = 1, 2, \ldots \tag{41}$$

$$F_i = (f_{i-1} - f_i)/x_0 \tag{42}$$

is a normalized nonlinear migration function involving $\theta_i\theta_j$ product terms [see Eq. (46)].

The corresponding transient adsorption–migration quasi-linear differential equation based on the kinetic theory is expressible in the following matrix form[5]:

$$-\left(\sum_{j=0}^{i-1}\dot{\theta}_j\right) = (A_{i-1}\theta_{i-1} - D_i\theta_i) - F^*(\theta_i, \theta_j), \qquad i = 1, 2, \ldots \tag{43}$$

where A_i and D_i are adsorption and desorption coefficients defined as follows.

The adsorption coefficient is

$$A_i = (\dot{n}/x_0)S_i \tag{44}$$

and the desorption coefficient is

$$D_i = (1/\tau_a)\exp(-E_i/RT) \tag{45}$$

In Eq. (42), F^* is a migration function, defined as

$$\begin{aligned}F^*(\theta_i, \theta_j) &= [F_{i-1}(\theta_{i-1}, f_{i-1}) - F_i(\theta_i, f_i)]\tau_{i-1}^{-1} \\ &= \sum_{j=i+1}^{\infty}(M_{i,j}\theta_i\theta_i - M_{j,i-1}\theta_j\theta_{i-1})\end{aligned} \tag{46}$$

where the migration coefficient is

$$M_{i,j} = (\beta_{i,j}/4\tau_a)\exp(-E_{mi}/RT) \tag{47}$$

where $\beta_{i,j}$ is a correction factor for migration probabilities for various combinations of layers i and j. These equations have indicated that Eq. (40) can be correlated with Eq. (43) despite the complicated

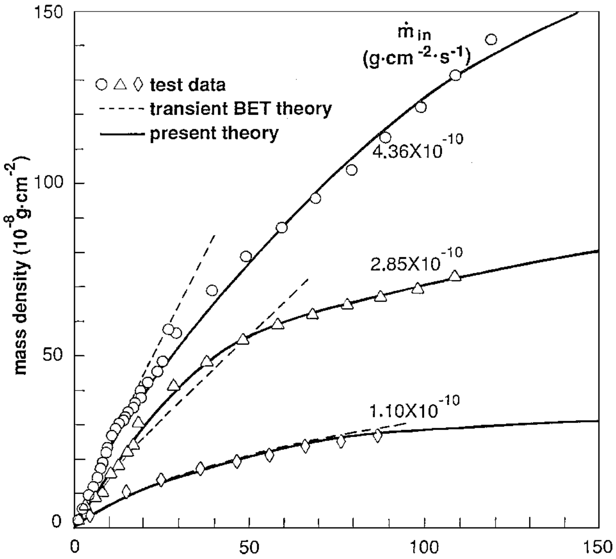

Fig. 3 Comparison of DC-704 oil vapor deposition data with transient adsorption–migration theory (reproduced from Ref. 5).

functional relationships. Even though extensive numerical details have not been carried out to correlate the two approaches quantitatively, it is quite conclusive qualitatively that these two approaches will yield the same solution.

The adsorption–migration model was verified by comparing the predictions with laboratory data for a DC-704 oil evaporation and condensation test. The laboratory test system included two quartz crystal microbalances (QCM) for deposition measurements and a sample cell for producing the source outgassing (or evaporation) rate, all properly arranged in a bell jar with liquid-nitrogen-cooled shields under high vacuum conditions (as low as 2×10^{-7} torr).[4,6,7] The two QCMs were symmetrically located so as to have the same view factor with the source cell; one QCM was set at 77 K to measure the total incident molecular flux, whereas the other QCM was set at various temperatures to measure the corresponding deposition rates (or sticking coefficients).[4] As discussed in Ref. 4, the warm QCM for the DC-704 test was set at 23.5°C, whereas the source temperature was allowed to vary, resulting in three incident fluxes, 4.36×10^{-10}, 2.85×10^{-10}, and 1.10×10^{-10} $\mathrm{g \cdot cm^{-2} \cdot s^{-1}}$ (Fig. 3). It is seen from Fig. 3, which is reproduced from Ref. 5, that excellent theory/data agreement is indicated for an early stage adsorption–migration problem. Note that, for higher deposit buildup, other molecular interaction effects would occur, and the problem is beyond the scope of the present model.

Conclusions

It has been proven in this analysis that the solution based on the statistical thermodynamic theory is equivalent to that based on the kinetic theory in describing the transient adsorption or adsorption–migration process. In either approach, each adsorbed layer is considered to be in an average statistically fluctuating state, and the derivative for the ith adsorbed layer depends only on its own layer and its nearest neighboring layers. Because the kinetic theory solutions have been verified by test data,[4,5] the corresponding solutions with the statistical thermodynamic theory are also valid. The present statistical thermodynamic solution, therefore, contributes to strengthening the theoretical foundation of the transient adsorption–migration model.

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