

Adsorption on heterogeneous surfaces. I. Evaluation of the energy distribution function via the Wiener and Hopf method

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A new method of evaluating the energy distribution function of sites participating in an adsorption process is presented. The method is based on the Wiener-Hopf technique for the solution of integral equations. The method is demonstrated through a derivation of the distribution functions for the generalized Freundlich and Dubinin-Radushkevich isotherms, and a new distribution function relating the local Langmuir isotherm to the Javanović isotherm is derived. A prescription for the analysis of experimental data is discussed.

I. HETEROGENEITY, DISTRIBUTION FUNCTIONS, AND THE INTEGRAL EQUATION OF ADSORPTION

The first theoretical investigations of physical and chemical processes in solids and other molecular complexes are generally made on models in which the material being considered is postulated to be uniform. Certain parameters, coupling constants, strengths of interaction, lattice spacings, relaxation times, etc., are given values which are constant in all parts of the sample being modeled. This homogeneity postulate is seldom satisfied in real systems. For this reason, in refined theories, more realistic models incorporate heterogeneities into certain distribution functions which are used to characterize the models.

Let us suppose that the variables which, through inhomogeneities, might extend over some range are $\alpha \equiv (\alpha_1, \alpha_2, \dots, \alpha_n)$; and that $Q \equiv (q_1, q_2, \dots, q_n)$ represents variables which can be externally controlled (temperature, pressure, external electric field, etc.) while making measurements on a system of interest. We then assume that a normalized distribution function of the α 's, $\rho(\alpha) \equiv \rho(\alpha_1, \alpha_2, \dots, \alpha_n)$, exists. Let us consider the case that an observed total response function $\Omega_i(Q)$, which is the outcome of some measurement, is a weighted average, with weight $\rho(\alpha)$, of a local response function $\Omega_L(Q, \alpha)$ of the heterogeneity parameters $\{\alpha_i\}$, i. e.,

$$\Omega_i(Q) = \int \Omega_L(Q, \alpha) \rho(\alpha) d^n \alpha. \quad (1)$$

Only in the case in which all α_i 's are sharply distributed is Ω_i equal to Ω_L .

In situations in which it is impossible to measure the distribution of the locally fluctuating variables, $\{\alpha_i\}$, the only way to obtain information on the distribution function $\rho(\alpha)$ is to make response measurements $\Omega_i(Q)$ over a wide range of $\{Q_i\}$. From knowledge of the local response function $\Omega_L(Q, \alpha)$ for fixed α , the unknown, $\rho(\alpha)$, might be determined by solving Eq. (1) as an integral equation. An alternative course of action is to choose some reasonable empirical form for $\rho(\alpha)$, which contains some arbitrary parameters and to select these parameters in such a manner as to give the best fit to the experimental data $\Omega_i(Q)$.

A number of specific systems for which data exist for a $\Omega_i(Q)$ and for which one wishes to determine a $\rho(\alpha)$ include (a) the determination of the location of multiple binding sites for small groups onto macromolecules,¹ (b) the activation energy distribution function in biomolecules,² (c) radiation damage annealing processes,³ (d) relaxation time distribution functions for electrical response of dielectrics and mechanical response of linear viscoelastic solids,⁴ (e) estimation of donor-acceptor distance distributions from fluorescence response,⁵ (f) the determination of surface area and porosity of solids,⁶ and (g) in adsorption studies.⁷⁻⁹ In the following we discuss heterogeneity in relation to adsorption experiments, but the methods we present are applicable to other systems which satisfy the necessary mathematical conditions. The characterization of surfaces is vital to the understanding of surface reaction, catalytic mechanisms, and other surface related phenomena. A powerful traditional method employed in surface studies is the measurement of adsorption isotherms, i. e., the relationships between coverage of a substrate surface by an adsorbant and the total pressure of the ambient, for fixed temperature. Various kinetic and statistical mechanical models as well as semiempirical methods have been developed for the evaluation of adsorption isotherms.⁷⁻¹⁰ Most theoretical treatments postulate a homogeneous substrate surface, which rarely exists. The surface heterogeneity to adsorption results from crystallographic irregularities (for example, cleavage steps, dislocations, and point defects) and contamination. In polycrystalline materials, nonuniformity is also caused by the exposure of a variety of crystal faces. Nonhomogeneous surfaces yield a spatially fluctuating potential energy for the adsorption of chemical species.

Such surfaces can be conceptually decomposed into patches which are to be pictured as homogeneous (homotactic) regions of dimensions large compared to atomic spacings but much smaller than the total surface area of the substrate. An equivalent alternative description is given in terms of adsorption sites which are defined as positions of potential energy minima with respect to motion perpendicular to an arbitrary reference plane at the site.¹¹ Consequently, the adsorption heterogeneity of a surface is modeled by a distribution

function of homotactic regions, or equivalently by a site distribution function. The total isotherm θ_t as a function of temperature and pressure is then a weighted superposition of the local isotherms, θ_L , of the patches

$$\theta_t = \int_{\epsilon_1}^{\epsilon_2} \theta_L(P, T; \epsilon) \rho(T; \epsilon) d\epsilon, \quad (2)$$

$$\int_{\epsilon_1}^{\epsilon_2} \rho(T; \epsilon) d\epsilon = 1, \quad (3)$$

where $\epsilon (\geq 0)$ is the adsorption energy, P and T are respectively the pressure and absolute temperature, and $\rho(T; \epsilon)$ is normalized distribution function of site energies.

The concept of adsorption on heterogeneous substrates can be traced to the pioneering work of Langmuir who proposed¹² an expression for the total isotherm. Since then, it has been the subject of numerous studies. Given the experimentally determined total isotherm θ_t and a theoretical local isotherms θ_L , there are two types of schemes for the evaluation of the distribution function ρ : one being empirical and the other requiring a direct integral inversion. In empirical treatments, a plausible, parametrically dependent distribution function is postulated, and the parameters are chosen to yield a best fit to the experimental data. Various functional forms for the distribution have been proposed (for example, exponential,¹³ Gaussian,⁸ exponential of a high-degree polynomial,¹⁴ log-normal,¹⁵ Maxwell-Boltzmann,¹⁶ and Poisson distributions¹⁷), and numerical fitting procedures have been developed. In the direct approach, the data (total isotherm, θ_t) is fitted by some function and the solution of the integral equation of adsorption [Eq. (2)] is attempted for an assumed form of the kernel, θ_L . In particular, we mention the Stieltjes^{18,19} and Fourier transform methods²⁰ in which θ_L was chosen to be a Langmuir isotherm, and the Laplace transform method²¹ in which Jovanovic's isotherm^{22,23} was used. In this context we note the condensation approximation method²⁴⁻²⁶ which is a "hybrid" of the empirical and direct approaches. This method consists of replacing the kernel in the above integral equation by a function of P which has a discontinuity where condensation occurs, thus permitting an analytical solution for the distribution function.

The inversion approach has the merit of not making *a priori* assumptions about the solution of the integral equation, hence it is a *direct* way of evaluating the distribution function. On the other hand, the inversion of Eq. (2) can be achieved by the above methods for only a few limited cases. In this paper we present the elements of a new technique for the solution of the integral equation of adsorption, based on the Wiener-Hopf method. We note that while in the following we restrict our discussion to the Langmuir isotherm as the kernel, and assume the integration to cover the entire half line $[0, \infty]$, thus requiring that the solution ρ belongs to the function space $L^1(0, \infty)$, the method is quite easily modified to treat kernels of a more general type and arbitrary limits of integration.²⁷ We commence with a brief description of the Wiener-Hopf method for the solution of integral equations in Sec. II. In Sec. III,

we give a detailed demonstration of the method for a few cases, to familiarize the reader with the technique. A brief discussion on its use for the analysis of experimental data is included in Sec. IV.

II. THE WIENER-HOPF METHOD²⁸⁻³⁰

Consider an integral equation on the half-line with a kernel $h(t, s)$ which depends upon the difference of the arguments

$$\int_0^\infty h(t-s)\rho(s)ds = f(t) \quad (0 \leq t < \infty). \quad (4)$$

When the given functions $h(t)$ and $f(t)$ in Eq. (4) belong to the classes L and L_+ , respectively, the solution to the above equation can be formally constructed as follows:

(i) let us define the Fourier transform of the kernel h to be

$$H(\lambda) = \int_{-\infty}^\infty e^{-it\lambda} h(t) dt. \quad (5)$$

and restrict ourselves to the case

$$H(\lambda) \neq 0 \quad (-\infty < \lambda < \infty), \quad (6)$$

(ii) if we perform the factorization

$$H^{-1}(\lambda) = \mathcal{H}_+(\lambda) \mathcal{H}_-(\lambda) \quad (-\infty < \lambda < \infty), \quad (7)$$

where $\mathcal{H}_+(\lambda)$ and $\mathcal{H}_-(\lambda)$ are functions holomorphic, respectively, in the interiors of the half-planes Π_+ (upper) and Π_- (lower) and not vanishing in the finite parts of their respective half-planes,

(iii) then the Fourier transform $\bar{\rho}(\lambda)$ of the unknown function can be written as

$$\bar{\rho}(\lambda) = \mathcal{H}_+(\lambda) P_+ [\mathcal{H}_-(\lambda) F(\lambda)], \quad (8)$$

where

$$F(\lambda) = \int_0^\infty e^{-it\lambda} f(t) dt, \quad (9)$$

and the operator P_+ is defined to be the principal value integral

$$P_+ \Phi(\lambda) = \frac{1}{2\pi i} \int \frac{\Phi(\mu)}{\mu - \lambda} d\mu \quad (\text{Im} \lambda > 0). \quad (10)$$

(iv) Finally the function $\rho(x)$ is obtained by Fourier inversion

$$\rho(x) = \int_{-\infty}^\infty e^{itx} \bar{\rho}(\lambda) d\lambda. \quad (11)$$

In the following section we apply this method.

III. DISTRIBUTION FUNCTIONS WITH A LANGMUIR KERNEL

In this chapter we assume that the local isotherm θ_L is the well known Langmuir isotherm^{12,31}

$$\theta_L(P, T; \epsilon) = [1 + P^{-1} a(T) \exp(-\epsilon/RT)], \quad (12)$$

where the meaning of $a(T)$ is clear from a statistical mechanics derivation of the Langmuir isotherm.^{31,32} The integral Eq. (2) reads now as

$$\theta_i(P, T) = \int_0^\infty [1 + P^{-1}a(T) \exp(-\epsilon/RT)]^{-1} \rho(\epsilon) d\epsilon. \quad (13)$$

The change of variable

$$P^{-1}a(T) \equiv e^y \quad (0 \leq y < \infty), \text{ and } x = \epsilon/RT, \quad (14)$$

puts Eq. (13) in the Wiener-Hopf form

$$\theta_i[a(T) e^y, T] = RT \int_0^\infty [1 + \exp(y-x)]^{-1} \rho(x) dx. \quad (15)$$

Now, we perform the steps (i) and (ii) of the Wiener-Hopf procedure outlined in the previous section. The Fourier transform of the kernel $h(u)$

$$h(u) = [1 + \exp(u)]^{-1}, \quad (16)$$

is, when $0 < \text{Im}k < 1$ ³³

$$H(k) = \int_{-\infty}^\infty h(u) \exp(-iku) du = \int_0^\infty [1+v]^{-1} v^{-ik-1} dv = \Gamma(-ik)\Gamma(1+ik). \quad (17)$$

where $\Gamma(z)$ is the gamma function of z .

Noting that $\Gamma(-ik)$ has poles at $k = -il$ ($l = 0, 1, 2, \dots$) and $\Gamma(1+ik)$ at $k = i(l+1)$ ($l = 0, 1, 2, \dots$) one can achieve the factorization of $H(k)^{-1}$ with

$$\mathcal{H}_+(k) = [\exp\phi(k)]/\Gamma(-ik), \quad (18a)$$

and

$$\mathcal{H}_-(k) = \{\exp[-\phi(k)]\}/\Gamma(1+ik). \quad (18b)$$

The function $\phi(k)$ is chosen by requiring that $\mathcal{H}_\pm(k)$ exhibit an algebraic behavior for large k . Using Stirling's formula for $\ln\Gamma(z)$ we obtain

$$\phi = ik. \quad (19)$$

We consider now several choices of the total adsorption isotherm.

A. Generalized Freundlich isotherm

The generalized Freundlich isotherm was suggested originally by Sips¹⁶ as an alternative to the Freundlich equation, which does not indicate saturation at high pressures. This isotherm can be written as

$$\theta_i(P, T) = [1 + P^{-1}a(T)]^{-c} \quad 0 < c < 1. \quad (20)$$

Using the transformation of variables in Eq. (14), one can write the one sided Fourier transform [Eq. (9)] of θ_i in Eq. (20) as

$$\Theta_i(k) = \int_0^\infty [1 + e^u]^{-c} \exp(-iku) du = \int_1^\infty (1+v)^{-c} v^{-ik-1} dv. \quad (21)$$

The above expression is identified as the integral representation of the hypergeometric function³⁴

$$\Theta_i(k) = [c + ik]^{-1} F(c, c + ik; c + ik + 1; -1) [\text{Im}(k) > c], \quad (22)$$

where

$$F(a, b; c; z) = \frac{\Gamma(c)}{\Gamma(a)\Gamma(b)} \sum_{n=0}^\infty \frac{z^n \Gamma(a+n)\Gamma(b+n)}{n! \Gamma(c+n)}. \quad (23)$$

Thus we obtain

$$\Theta_i(k) = \frac{1}{\Gamma(c)} \sum_{n=0}^\infty \frac{(-1)^n \Gamma(c+n)}{n! (c+n+ik)}. \quad (24)$$

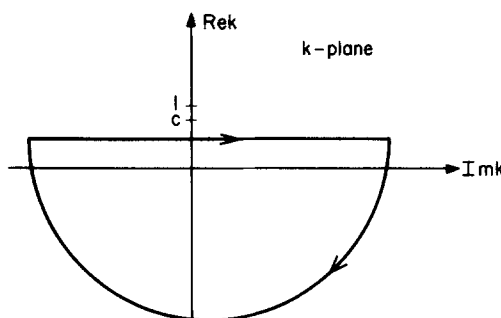


FIG. 1. The contour of intergration used in obtaining the projection P_+ , in Eq. (25).

The projection P_+ , defined by Eq. (10), can now be performed using the contour shown in Fig. 1, yielding

$$P_+[\mathcal{H}_-(\lambda)\Theta_i(\lambda)] = \frac{\exp(-i\lambda)}{\Gamma(c)\Gamma(1+i\lambda)} \sum_{n=0}^\infty \frac{(-1)^n \Gamma(c+n)}{n! (c+n+i\lambda)}. \quad (25)$$

We now construct the Fourier transform of ρ [see Eq. (8)] by multiplying Eq. (25) by $\mathcal{H}_+(\lambda)$, given in Eq. (18a), and performing the Fourier inversion [step (iv), Eq. (11)]:

$$\rho(x) = \frac{1}{RT\Gamma(c)} \sum_{n=0}^\infty \frac{(-1)^n \Gamma(c+n)}{n!} \int_{-\infty}^\infty \frac{\exp(i\lambda x) d\lambda}{(c+n+i\lambda)\Gamma(1+i\lambda)\Gamma(-i\lambda)}. \quad (26)$$

Closing the contour in the upper half-plane we get

$$\rho(x) = [RT\Gamma(c)]^{-1} \sum_{n=0}^\infty \frac{(-1)^n \exp[-(c+n)x]}{\Gamma[1-(c+n)]} \quad (27)$$

Using the relation

$$\Gamma(x)\Gamma(1-x) = \frac{\pi}{\sin(\pi x)}, \quad (28)$$

we can rewrite Eq. (25) in the form

$$\rho(x) = \frac{\sin(\pi c) \exp(-cx)}{\pi RT} \left[1 + \Gamma(1-c) \sum_{n=1}^\infty \frac{(-1)^n \exp(-nx)}{n! \Gamma[1-(c+n)]} \right]. \quad (29)$$

We note now that the term in square brackets in the above equation is the asymptotic expansion of the function

$$\exp(cx) [\exp(x) - 1]^{-c}. \quad (30)$$

By replacing the sum in Eq. (29) by this expression and using Eq. (14) we obtain

$$\rho(\epsilon) = \frac{\sin(\pi c)}{\pi RT} [\exp(\epsilon/RT) - 1]^{-c}. \quad (31)$$

This result is identical to the one derived by Sips using the Stieltjes transform.¹⁸

B. Dubinin-Radushkevich isotherm.

The Dubinin-Radushkevich isotherm is given by³⁵

$$\theta_i(P, T) = \exp\{-B[RT \ln(P_0/P)]^2\}, \quad (32)$$

where P_0 is the saturation vapor pressure of the adsorbed gas at the ambient temperature T , and B is a constant. Substituting for P from Eq. (14) and defining $A \equiv B(RT)^2$ and $C \equiv \ln[P_0/a(T)]$ we obtain

$$\theta_t(y, T) = \exp[-A(C+y)^2]. \quad (33)$$

The one-sided Fourier transform of Eq. (33) is

$$\Theta_t(k) = e^{-AC^2} \int_0^\infty \exp[-Ay^2 - y(2CA + ik)] dy. \quad (34)$$

Using a known definite integral³⁶ we find

$$\int_0^\infty x^{\nu-1} \exp(-\beta x^2 - \gamma x) dx = (2\beta)^{-\nu/2} \exp(\gamma^2/8\beta) \Gamma(\nu) D_{-\nu}(\gamma/\sqrt{2\beta});$$

$$\operatorname{Re} \beta > 0, \operatorname{Re} \nu > 0, \quad (35)$$

and the relation between the parabolic cylinder function $D_{-1}(z)$ and the error function $\operatorname{erfc}(z)$,

$$D_{-1}(z) = (\pi/2)^{1/2} \exp(z^2/4) \operatorname{erfc}(z/2^{1/2}), \quad (36)$$

we get for $\Theta_t(k)$ the following expression:

$$\Theta_t(k) = \frac{1}{2} (\pi/A)^{1/2} \exp\left[-AC^2 + \frac{(2CA + ik)^2}{4A}\right] \times \operatorname{erfc}[(2CA + ik)/2A^{1/2}]. \quad (37)$$

Using \mathcal{K}_+ , given by Eq. (18b), the projection P_+ can now be performed yielding

$$P_+[\mathcal{K}_-(\lambda) \theta_t(\lambda)] = \frac{\sqrt{\pi} \exp\left[-AC^2 + \frac{(2CA + i\lambda)^2}{4A}\right] \operatorname{erfc}[(2CA + i\lambda)/2A^{1/2}]}{2\Gamma(1 + i\lambda)} \quad (38)$$

Multiplication by $\mathcal{K}_+(\lambda)$, given in Eq. (18a), and Fourier inversion yield after some algebraic manipulation the following inverse Laplace transform expression for $\rho(x)$,

$$\rho(x) = \frac{\exp(-AC^2 - 2CAx)}{i\sqrt{\pi RT}} \times \int_{-i\infty + C'}^{+i\infty + C'} \sin[2\pi(\sqrt{A}u - CA)] \exp(u^2 + 2\sqrt{A}ux) \operatorname{erfc}(u) du, \quad (39)$$

where $C' = CA^{1/2}$.

Using the known Laplace inversion formula³⁷

$$\mathcal{L}^{-1}[e^{ap^2} \operatorname{erfc}(a^{1/2}p)] = (\pi a)^{-1/2} \exp(-t^2/4a), \quad (40)$$

we get

$$\rho(\epsilon) = (\pi RT)^{-1} \exp[A\pi^2 - B(CRT)^2 - 2BCRT\epsilon - B\epsilon^2] \times \sin[2\pi BRT(C/RT + \epsilon)]. \quad (41)$$

When $p_0 = a(T)$, $C = \ln[p_0/a(T)]$ vanishes and

$$\rho(\epsilon) = (\pi RT)^{-1} \exp[-B\{\epsilon^2 - (\pi RT)^2\}] \sin(2\pi BRT\epsilon), \quad (42)$$

which is identical to the result obtained by the Stieltjes transform technique,³⁸ and by another method.³⁹

C. Jovanovic isotherm

Recently, Jovanović proposed a new isotherm equation,^{22,23} In the adsorption model considered by Jovanović, two new types of collisions are taken into account in addition to the processes which lead to the Langmuir isotherm. These additional processes are collisions between bulk and adsorbed molecules. This isotherm was employed recently²¹ in the analysis of experimen-

tal data of the adsorption of argon on rutile.⁴⁰ The distribution function obtained in the analysis based on a Jovanović local isotherm differs from those obtained in previous studies based on a Langmuir local isotherm.^{40,41} These differences were attributed²¹ to the differences in the physical mechanisms leading to the two isotherms. These involve adsorption sites associated with a low adsorption energy which, though formally occupied, are, in fact, free because of the high energy of the molecules covering them. In the present section we show that the Jovanović isotherm can in fact be derived from Langmuir's local isotherm via the integral equation for heterogeneous adsorption. In the following we derive the corresponding distribution function.

The Jovanović isotherm can be written as

$$\theta_t(P, T; \epsilon') = 1 - \exp[-(P/\alpha) \exp(\epsilon'/RT)], \quad (43)$$

where α depends on temperature. As can be shown by an expansion of Eq. (43) in powers of the pressure and taking the limit $P \rightarrow 0$, α is the proportionality constant in Henry's law. By changing variables according to Eq. (14) we can write the one-sided Fourier transform of Eq. (43) as

$$\Theta_t(k) = \int_0^\infty \{1 - \exp[-C \exp(-u)]\} \exp(-iku) du = \int_0^\infty \exp(-iku) du - \int_0^1 v^{ik-1} \exp(-Cv) dv \equiv I_1 - I_2, \quad (44a)$$

where

$$C(T) = a(T)/\alpha(T). \quad (44b)$$

We make use of the following known⁴² integral representation of the incomplete gamma function $\gamma(\alpha, \beta)$:

$$\int_0^u x^{\nu-1} \exp(-\mu x) dx = \mu^{-\nu} \gamma(\nu, \mu u); \quad (\operatorname{Re} \nu > 0), \quad (45)$$

which yields

$$I_2 = C^{-ik} \gamma(ik, C); \quad (\operatorname{Im} k < 0). \quad (46)$$

The function $\gamma(a, x)$ is in turn related to the degenerate hypergeometric function $\Phi(a, b; z)$ by⁴³

$$\gamma(a, x) = \frac{x^a}{a} \Phi(a, 1+a; -x), \quad (47)$$

where

$$\Phi(a, b; z) = \sum_{n=0}^{\infty} \frac{\Gamma(a+n)\Gamma(b)z^n}{\Gamma(a)\Gamma(b+n)n!}. \quad (48)$$

Finally we get for Θ_t the following expression:

$$\Theta_t(k) = -\sum_{n=1}^{\infty} \frac{(-1)^n C^n}{n!(n+ik)}; \quad (\operatorname{Im} k < 0). \quad (49)$$

Following the steps of the Wiener-Hopf procedure and using Eqs. (8)–(11), (18) and (49) we obtain the following inversion formula:

$$\rho(x) = -(RT)^{-1} \sum_{n=1}^{\infty} \frac{(-1)^n C^n}{n!} \int_{-\infty}^{\infty} \frac{\exp(i\lambda x) d\lambda}{(n+i\lambda)\Gamma(-i\lambda)\Gamma(1+i\lambda)}. \quad (50)$$

The integral in the above equation can be written as

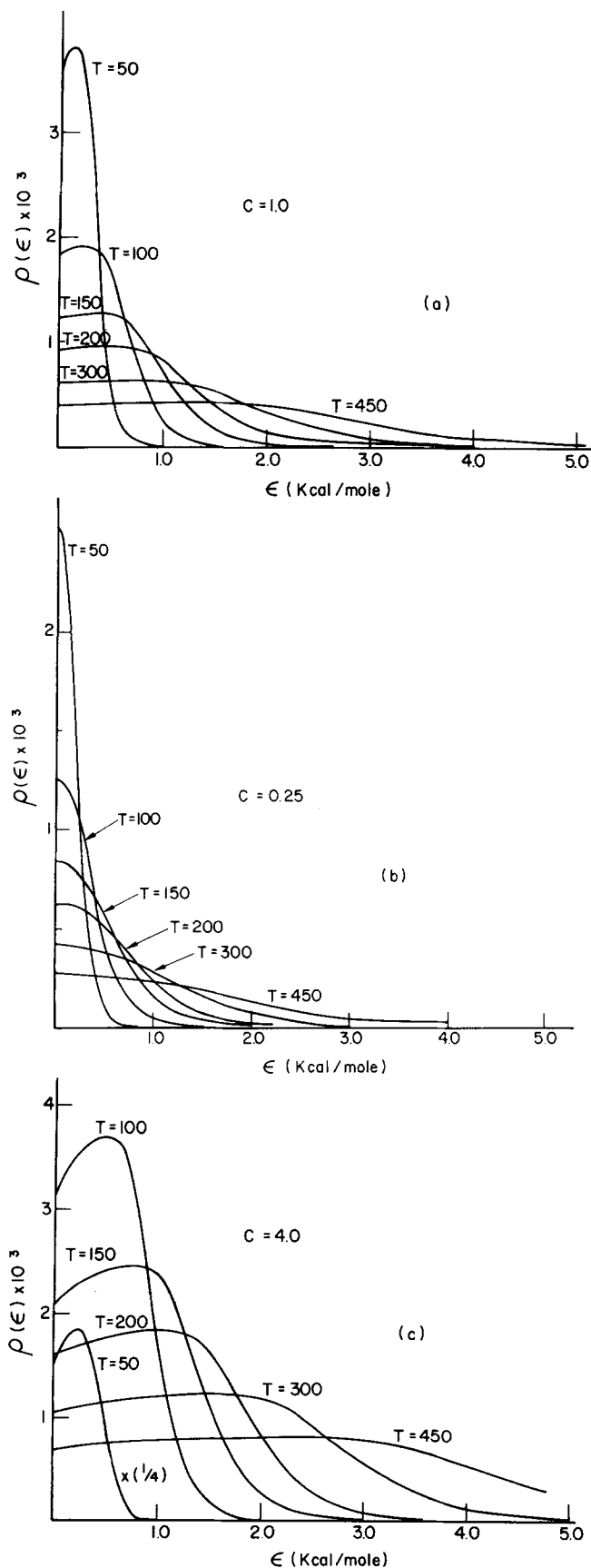


FIG. 2. The distribution function $\rho(\epsilon)$, relating the Langmuir local isotherm to the Jovanović isotherm. Curves are shown for three values of C [Eq. (44)] taken as a constant, independent of temperature (a, $C=1$; b, $C=0.25$; c, $C=4.0$). For each value of C , the distribution function for several temperature is shown.

$$\pi^{-1} \sum_{k=0}^{\infty} \frac{\pi^{2k+1}}{(2k+1)!} \int_{-\infty}^{\infty} \frac{\lambda^{2k+1} \exp(i\lambda x)}{in - \lambda} d\lambda = -2e^{-nx} \sinh(n\pi). \quad (51)$$

After some algebraic manipulations, the normalized distribution function which relates the local Langmuir isotherm to the Jovanović isotherm can be written as

$$\rho(\epsilon) = N(RT)^{-1} \{ \exp[-r \exp(-\epsilon/RT)] - \exp[-s \exp(-\epsilon/RT)] \}, \quad (52)$$

where the normalization constant N is given by

$$N = [\text{Ei}(r) - \text{Ei}(s)]^{-1}, \quad (53)$$

where $\text{Ei}(x)$ is the exponential integral function and $r = C \exp(\pi)$, $s = C \exp(-\pi)$. The above distribution function for several values of the temperature is shown in Fig. 2.

IV. ANALYSIS OF EXPERIMENTAL DATA

In a usual isotherm study, the coverage $\theta_t(P, T)$ is recorded as a function of the total ambient pressure for constant temperature T . Given such isotherm data, we can find a least-square fit to it,⁴⁴ defined by the coefficient $C_n(T)$,

$$\theta_t(P, T) = \sum_{n=1}^M C_n(T) P^n. \quad (54)$$

Note that we start the series at $n=1$ in order to satisfy Henry's law. A simple transformation of variables [Eq. (14)] yields

$$\theta_t(y, T) = \sum_{n=1}^M [a(T)]^n C_n(T) e^{-ny}. \quad (55)$$

The one sided Fourier transform of Eq. (55) can be written as

$$\Theta_t(k, T) = \sum_{n=1}^M [a(T)]^n \frac{C_n(T)}{n + ik}; \quad (n > \text{Im}k). \quad (56)$$

Using the factorization of the transform of the Langmuir kernel [Eqs. (18)] and performing the operations indicated in Eqs. (8), (10), and (11) we find the following inversion formula for the distribution function $\rho(x)$

$$\rho(x) = (RT)^{-1} \sum_{n=1}^M [a(T)]^n C_n(T) \int_{-\infty}^{\infty} \frac{\exp(i\lambda x) d\lambda}{(n + i\lambda)\Gamma(-i\lambda)\Gamma(1 + i\lambda)}. \quad (57)$$

This integral is the same as the one in Eq. (50). Finally we get

$$\rho(\epsilon) = N(RT)^{-1} \sum_{n=1}^M [a(T)]^n C_n(T) \sinh(n\pi) \exp\left(\frac{-n\epsilon}{RT}\right), \quad (58)$$

where N is a normalization factor equal to

$$N = \left\{ \sum_{n=1}^M n^{-1} [a(T)]^n C_n(T) \sinh(n\pi) \right\}^{-1}. \quad (59)$$

The average energy associated with this distribution function is given by

$$\bar{\epsilon} = \int_0^{\infty} \epsilon \rho(\epsilon) d\epsilon = NRT \sum_{n=1}^M n^{-2} [a(T)]^n (T) \sinh(n\pi) \quad (60)$$

From Eqs. (54), (58)–(60) it is seen that the coefficients $C_n(T)$ [Eq. (54)] determine the distribution function. Furthermore, distribution functions relating the Langmuir isotherm to other isotherms [like the one de-

rived in section IIIC, relating the Langmuir and Jovanović isotherms, Eqs. (52) and (53)] can be incorporated to achieve an analysis based on local isotherms other than the Langmuir one. A detailed discussion of the application of the method to the analysis of experimental data is reported elsewhere.²⁷

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