

Kinetics of Gas Adsorption on Strongly Heterogeneous Solid Surfaces: A Statistical Rate Theory Approach

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Abstract—A fundamental theoretical investigation is carried out on the applicability of the Condensation Approximation (CA) method of generalizing the theoretical description of the kinetics of gas adsorption/desorption on/from energetically heterogeneous solid surfaces. Our investigation implies that the commonly observed Elovich's behavior is a consequence of carrying out kinetic experiments at conditions not far from equilibrium. This striking result seems to suggest that the applicability of that popular approximation deserves further fundamental study.

Key words: Surface Energetic Heterogeneity, Statistical Rate Theory, Condensation Approximation, Adsorption Kinetics

INTRODUCTION

The overwhelming majority of the solid surfaces in studies of adsorption processes are energetically heterogeneous. This energetic heterogeneity is a consequence of the geometric heterogeneity which is an intrinsic feature of all real solid surfaces. Recently, Rudzinski and Panczyk [2001a, b] have published two papers that studied the fundamental relations between the geometric and energetic surface heterogeneities.

The effects of the energetic heterogeneity on adsorption equilibria have been the matter of hundreds of publications, several reviews and few monographs [Do, 1998; Jaroniec and Madey, 1988; Rudzinski and Everett, 1992; Kim et al., 2001]. At the same time, little progress could be seen, until very recently, in our understanding of the features of the kinetics of adsorption on energetically heterogeneous solid surfaces. Meanwhile, many experimental observations were reported suggesting that as in the case of adsorption equilibria, the surface energetic heterogeneity has pronounced effect of the features of adsorption kinetics. It could clearly be seen in studies of gas adsorption on strongly heterogeneous solid surfaces [Low, 1960; Ryu et al., 2001].

It has been known for a long time that, when in adsorption systems the adsorption equilibria are described by Temkin empirical equation, then the adsorption kinetics is described well by the Elovich empirical equation. This was observed commonly in adsorption systems with strongly heterogeneous solid surfaces - the catalysts' surfaces, for instance. Later on a theoretical explanation for that was given, based on a Langmuiric model of adsorption on surfaces characterized by a rectangular adsorption energy distribution. It is known that this function is a crude but also an efficient approximation for the actual adsorption energy distributions characterizing

strongly energetically heterogeneous solid surfaces. As far as the adsorption kinetics is concerned, that proof was first based on applying the classical TAAD (Theory of Activated Adsorption/Desorption) approach [Aharoni and Tompkins, 1970; Elovich and Zabrova, 1939; Kharakorin and Elovich, 1936; Rudzinski and Panczyk, 1999].

The TAAD approach developed at the beginning of the previous century has commonly been applied, but also common were reports on its limited success to describe the kinetics of adsorption in the real adsorption systems. The new SRT (Statistical Rate Theory) approach developed at the beginning of the 1980's [Ward et al., 1982] has revealed one of the important reasons for that. Namely, the classical TAAD approach did not refer to the technical conditions at which the adsorption kinetics is studied. The new SRT approach shows that the construction of the experimental set-up affects the behavior of the observed adsorption kinetics [Elliott and Ward, 1997a, b].

While considering that problem in our previous publications we distinguished the three extreme conditions at which the experiments may be carried out. We classified such systems as "volume dominated" (V), "solid dominated" (S) and "equilibrium dominated" (E) ones. In our previous publications we have studied the behavior of the adsorption kinetics at these three extreme conditions in adsorption on homogeneous solid surfaces [Rudzinski and Panczyk, 2002], and on a moderately heterogeneous surfaces characterized by a quasi-gaussian adsorption energy distribution [Rudzinski and Panczyk, 2000, 2002b, c, 2003].

For adsorption on strongly heterogeneous surfaces, we studied only the case of the "equilibrium dominated" systems. The purpose of the present publication is to study the behavior of the kinetics of adsorption on strongly heterogeneous surfaces, monitored at conditions when the system is "volume" and "solid" dominated. In the case of strongly heterogeneous solid surfaces, the surface energetic heterogeneity may be represented by the simple constant adsorption energy distribution. This is a very fortunate circumstance from the point of view of carrying out theoretical studies of some fundamental features of the kinetics of adsorption on energetically heter-

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‡This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

ogeneous surfaces. While carrying out such studies, we arrived at very interesting conclusions about the necessity of reconsidering some of the applied theoretical approaches.

THEORY

Since the beginning of the 1940's, the so-called integral equation has most commonly been used to study the equilibria of gas adsorption on energetically heterogeneous solid surfaces. [Do, 1998; Jaroniec and Madey, 1988; Rudzinski and Everett, 1992] The experimentally monitored average (fractional) surface coverage $\theta_i^{(e)}$ at temperature T, and at the equilibrium pressure $p^{(e)}$ has been expressed as follows,

$$\theta_i^{(e)}(p^{(e)}, T) = \int_{\varepsilon_1}^{\varepsilon_m} \theta^{(e)}(\varepsilon, p^{(e)}, T) \chi(\varepsilon) d\varepsilon \quad (1)$$

where $\chi(\varepsilon)$ is the distribution of adsorption sites among the corresponding values of the adsorption energy ε , and ε_1 and ε_m are the lowest and the highest values of ε , respectively, existing on the investigated solid surfaces. Further, $\theta^{(e)}(\varepsilon, p^{(e)}, T)$ is the fractional coverage of adsorption sites having adsorption energy ε . Most commonly, the Langmuir isotherm equation was applied to represent $\theta^{(e)}(\varepsilon, p^{(e)}, T)$,

$$\theta^{(e)} = \frac{\exp\left(\frac{\varepsilon - \varepsilon_c}{kT}\right)}{1 + \exp\left(\frac{\varepsilon - \varepsilon_c}{kT}\right)} \quad (2)$$

where

$$\varepsilon_c = -kT \ln K p^{(e)} \quad (2a)$$

In Eq. (2a), K is the so-called Langmuir constant, and k is Boltzmann constant. When $T \rightarrow 0$, Eq. (2) becomes the step function $\theta_c(\varepsilon_c, T)$,

$$\theta_c(\varepsilon_c, T) = \begin{cases} 0 & \text{for } \varepsilon < \varepsilon_c \\ 1 & \text{for } \varepsilon \geq \varepsilon_c \end{cases} \quad (3)$$

Replacing $\theta^{(e)}$ by θ_c in Eq. (1) has been known as the CA (Condensation Approximation) approach. It has been shown that the essential condition for the CA approach to be applicable is not necessarily the limit $T \rightarrow 0$. The CA approach can also be successfully applied at finite temperatures, when the variance of $\chi(\varepsilon)$ is essentially larger than that of the derivative $(\partial\theta^{(e)}/\partial\varepsilon)$ [Rudzinski and Everett, 1992].

In the case of strongly heterogeneous solid surfaces, the CA (Condensation Approximation) approach is a simple approach to describe the adsorption equilibria and kinetics. The equilibrium adsorption isotherm $\theta_i^{(e)}$ is then given by the equation [Rudzinski and Everett, 1992],

$$\theta_i^{(e)}(p^{(e)}, T) = \int_{\varepsilon_1}^{\varepsilon_m} \chi(\varepsilon) d\varepsilon \quad (4)$$

Very recently Rudzinski and Panczyk [2003] have shown that such integral equations can also be formulated for non-equilibrium conditions.

$$\theta_i(p, T, t) = \int_{\varepsilon_c(t)}^{\varepsilon_m} \chi(\varepsilon) d\varepsilon \quad (5)$$

The function ε_c becomes then a function of temperature T, the non-equilibrium pressure p, and time t. The explicit form of that function depends on the assumed model of adsorption, and on the conditions at which the kinetic experiment is carried out. The fact that

the monitored kinetics depends on the technical parameters of an experimental set-up is one of the fundamental discoveries of this new SRT approach. As in our previous publications we consider here the following two extreme situations.

(1) The features of a gas/solid system are “*volume dominated*”, i.e., the amount of the adsorbate in the gas phase above the surface is much larger than the portion adsorbed. In that case, after the system is isolated and equilibrated, the gas pressure p does not change much, so that $p^{(e)} \approx p$.

(2) The features of a gas/solid system are “*solid dominated*”. In this case the adsorbed amount is much larger than the amount in the bulk gas phase, so that after isolating the system and equilibrating, θ remains practically unchanged and $\theta \approx \theta^{(e)}$.

While assuming Langmuir model of adsorption, Rudzinski and Panczyk have developed the explicit expressions for the functions $\varepsilon_c(p, T, t)$, corresponding to the two above considered physical situations.

For the “*volume dominated*” (V) system, the $\varepsilon_c(t)$ function takes the following form,

$$\varepsilon_c^{(V)}(T, p, t) = kT \ln \left[\frac{1}{Kp} + \left(e^{\frac{\varepsilon_m}{kT}} - \frac{1}{Kp} \right) \exp(-2pK'_g t) \right] \quad (6)$$

whereas for the “*solid dominated*” (S) system, it reads,

$$\varepsilon_c^{(S)}(T, p, t) = \frac{1}{2} kT \ln \left[\frac{1}{(Kp)^2} + \left(e^{\frac{2\varepsilon_m}{kT}} - \frac{1}{(Kp)^2} \right) \exp(-4pK'_g t) \right] \quad (7)$$

where ε_m^* is the value of $\varepsilon_c(t)$ at $t=0$ and K'_g is the equilibrium exchange rate [Elliott and Ward, 1997a, b; Ward et al., 1982; Rudzinski and Panczyk, 2002a, b, c]. When at $t=0$, $\theta=0$, then $\varepsilon_m^* = \varepsilon_m$, but in general $\varepsilon_m^* < \varepsilon_m$, because outgassing of the sample always leaves a certain amount of adsorbate on the surface. Therefore $\varepsilon_m^* = -kT \ln Kp^*$, where p^* is the pressure at which the outgassing was carried out.

Now, let $\chi(\varepsilon)$ be the rectangular adsorption energy distribution,

$$\chi(\varepsilon) = \begin{cases} \frac{1}{\varepsilon_m - \varepsilon_1} & \text{for } \varepsilon_1 \leq \varepsilon \leq \varepsilon_m \\ 0 & \text{elsewhere} \end{cases} \quad (8)$$

Then,

$$\theta_i^{(e)}(p^{(e)}, T) = \frac{\varepsilon_m}{\varepsilon_m - \varepsilon_1} - \frac{\varepsilon_c}{\varepsilon_m - \varepsilon_1} = \frac{\varepsilon_m}{\varepsilon_m - \varepsilon_1} + \frac{kT}{\varepsilon_m - \varepsilon_1} \ln K p^{(e)} \quad (9)$$

Eq. (9) is the well-known Temkin isotherm, known also as the UNILAN isotherm in adsorption literature [Do, 1998]. The observed kinetic isotherm $\theta_i(p, T, t)$ will take the form,

$$\theta_i(p, T, t) = \theta_i^{(V)}(p, T, t) = \frac{\varepsilon_m}{\varepsilon_m - \varepsilon_1} - \frac{\varepsilon_c^{(V)}(t)}{\varepsilon_m - \varepsilon_1} \quad (10)$$

for the V-systems, and for the S-systems,

$$\theta_i(p, T, t) = \theta_i^{(S)}(p, T, t) = \frac{\varepsilon_m}{\varepsilon_m - \varepsilon_1} - \frac{\varepsilon_c^{(S)}(t)}{\varepsilon_m - \varepsilon_1} \quad (11)$$

respectively. In the next section we will study the behavior of the kinetic isotherms $\theta_i^{(V)}(t)$, and $\theta_i^{(S)}(t)$ describing the kinetics of adsorption in *volume* and in the *solid* dominated systems.

NUMERICAL RESULTS AND DISCUSSION

The generalization by us of the integral equation formalism to describe the kinetics of adsorption/desorption on/from energetically heterogeneous solid surfaces may appear to be a powerful and attractive tool for many researchers. So far, we have discussed only one example of the applicability of that new description formalism, to the systems characterized by the quasi-gaussian adsorption energy distribution leading to the Langmuir-Freundlich isotherm equation for adsorption equilibria. Such energy distribution is typical for moderately heterogeneous solid surfaces. Then, it has been also known for a long time, that in the case of strongly heterogeneous surfaces, the rectangular adsorption energy distribution (8) efficiently represents the features of such solid surfaces.

However, whichever is the form of the adsorption energy distribution, the fundamental features of adsorption mechanism and effects of the conditions in which the experiment is carried out are inherent in the form of the function $\epsilon_c(t, T, p)$. We start, therefore, our investigation by carrying out some model investigations showing some fundamental features of that function.

For that purpose we rewrite Eqs. (6) and (7) to the following form,

$$\epsilon_c^{(v)}(T, p, t) = -kT \ln Kp + kT \ln \left[1 + \left(Kp e^{\frac{\epsilon_m^*}{kT}} - 1 \right) \exp(-2pK_g^*t) \right] \quad (12)$$

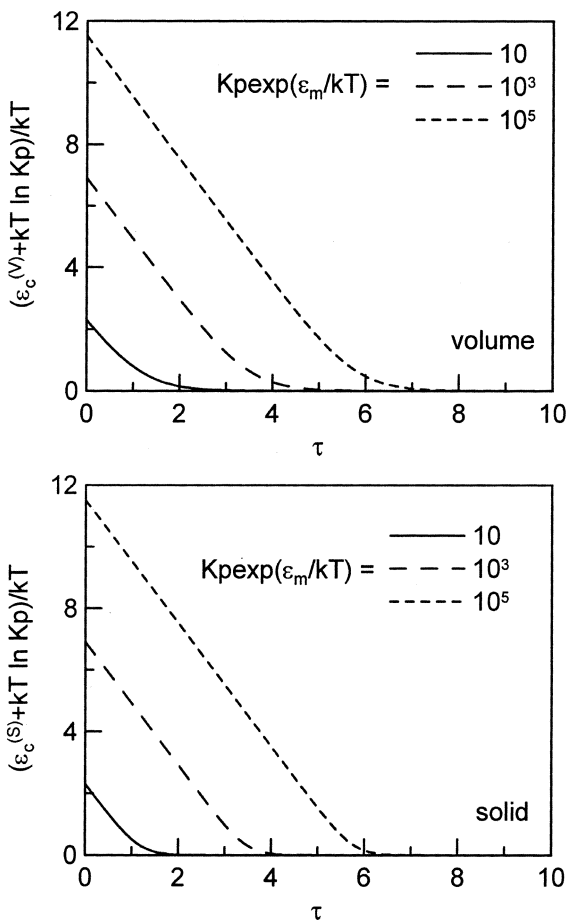


Fig. 1. The features of the functions $\epsilon_c^{(v)}$ and $\epsilon_c^{(s)}$ for a few values of the parameter $Kp \exp(\epsilon_m/kT)$. It is assumed that $\epsilon_m^* = \epsilon_m$, i.e. there is no pre-adsorbed amount on the surface.

$$\epsilon_c^{(s)}(T, p, t) = -kT \ln Kp + \frac{1}{2} kT \ln \left[1 + \left((Kp)^2 e^{\frac{2\epsilon_m^*}{kT}} - 1 \right) \exp(-4pK_g^*t) \right] \quad (13)$$

We can see that the $\epsilon_c(T, p, t)$ functions consist of a constant term $-kT \ln Kp$, and the time dependent terms which are functions of the dimensionless time $\tau = pK_g^*t$, and of the parameter $Kp \exp(\epsilon_m^*/kT)$.

In Fig. 1 we present model investigations of the functions $\epsilon_c^{(v)}$ and $\epsilon_c^{(s)}$ showing their basic features. Looking at the Fig. 1, we can see that both functions $\epsilon_c^{(v)}$ and $\epsilon_c^{(s)}$ are fairly linear for almost all values of time. Also, they are very similar to each other.

Looking to Eqs. (10) and (11), we can see that this is now the function $\epsilon_c(t)$ which essentially governs the behavior of the monitored function $\theta(t)$. While assuming the gaussian-like adsorption energy distribution we could not clearly say, to which extent the features of the experimentally monitored function $\theta(t)$ are due to the form of the adsorption energy distribution and which are due to some fundamental features of adsorption kinetics inhered in the function $\epsilon_c(t)$. This time the features of $\theta(t)$ are predominantly governed by the features of the function $\epsilon_c(t)$. To see these features, we have carried out some illustrative calculations, which are shown in Fig. 2. We have shown there the $\theta(t)$ in terms of both the reduced time τ and $\ln \tau$. The reason for that was the following.

It has been a common procedure in adsorption literature to correlate the kinetic isotherms of adsorption on heterogeneous solid surfaces, by using the Elovich empirical equation.

$$\frac{d\theta}{dt} = a e^{-b\theta} \quad (14)$$

where a and b are some constants characteristic for an adsorption system under investigation. Integration of Eq. (14) with the boundary condition $\theta(t=0)=0$, yields,

$$\theta_t = \frac{1}{b} \ln[abt + 1] \quad (15)$$

Eq. (15) would suggest that θ should be a fairly linear function of $\ln t$. This was observed in many adsorption systems. In some of our publications we studied the theoretical origin of this linear dependence in the case of equilibrium dominated systems. It was confirmed by our study that this is the rectangular adsorption energy distribution which is responsible for that linear dependence of θ vs. $\ln t$. Here, we study this problem for the systems which may be far from equilibrium and are either solid or volume dominated ones.

Kinetic isotherms of adsorption for the solid and volume dominated systems can be obtained by combining Eqs. (10), (11) and Eqs. (12), (13). They have the following explicit forms.

$$\theta_t^{(v)} = \frac{kT}{\epsilon_m - \epsilon_1} \ln \frac{Kp \exp\left(\frac{\epsilon_m}{kT}\right)}{1 + \left(Kp \exp\left(\frac{\epsilon_m^*}{kT}\right) - 1 \right) \exp(-2pK_g^*t)} \quad (16)$$

$$\theta_t^{(s)} = \frac{kT}{2(\epsilon_m - \epsilon_1)} \ln \frac{(Kp)^2 \exp\left(\frac{2\epsilon_m}{kT}\right)}{1 + \left((Kp)^2 \exp\left(\frac{2\epsilon_m^*}{kT}\right) - 1 \right) \exp(-4pK_g^*t)} \quad (17)$$

While analyzing the results presented in Fig. 2 we discover that the Eqs. (16) and (17) predict a much different behavior than the em-

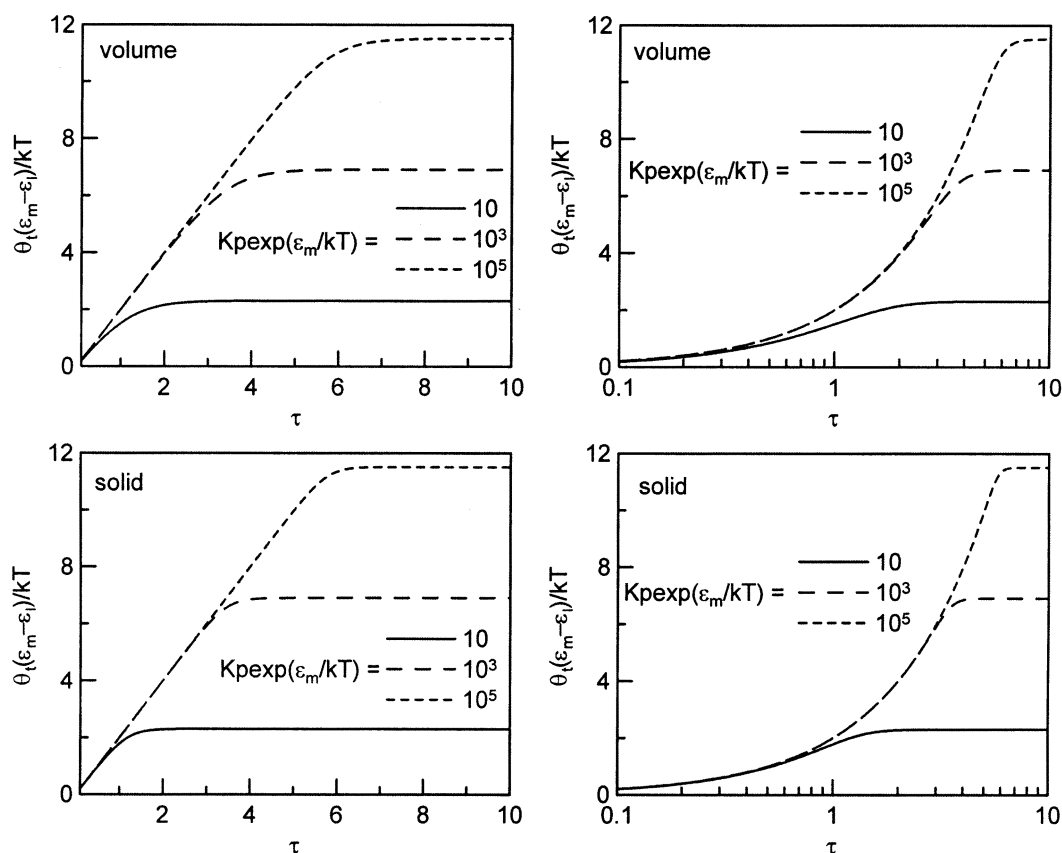


Fig. 2. Kinetic isotherms of both volume and solid dominated systems for some values of the parameter $Kp\exp(\epsilon_m/kT)$. Here it is assumed that the pre-adsorbed amount does not exist, i.e., $\epsilon_m^* = \epsilon_m$.

pirical Elovich Eq. (15). The isotherms plotted in linear coordinates are evidently linear, whereas when we plot them in linear-logarithmic coordinates they are no longer linear. It is in contradiction with the Elovich equation, which is linear just in linear-logarithmic coordinates.

However, our earlier analysis [Rudzinski and Panczyk, 1999] of the equilibrium dominated system revealed that the Elovich equation can be developed by using the SRT approach and Condensation Approximation for the rectangular adsorption energy distribution. The $\epsilon_c^{(E)}$ function for the equilibrium dominated system can be expressed as follows,

$$\epsilon_c^{(E)} = -kT \ln Kp + kT \ln \frac{Kp e^{\frac{\epsilon_m^*}{kT}} - 1 + \left(1 + Kp e^{\frac{\epsilon_m^*}{kT}}\right) \exp(4pK_s' t)}{1 - Kp e^{\frac{\epsilon_m^*}{kT}} + \left(1 + Kp e^{\frac{\epsilon_m^*}{kT}}\right) \exp(4pK_s' t)} \quad (18)$$

So, the corresponding kinetic isotherm of adsorption leads to,

$$\theta_t^{(E)} = \frac{kT}{\epsilon_m - \epsilon_1} \ln \frac{Kp e^{\frac{\epsilon_m^*}{kT}} \left[1 - Kp e^{\frac{\epsilon_m^*}{kT}} + \left(1 + Kp e^{\frac{\epsilon_m^*}{kT}}\right) \exp(4pK_s' t) \right]}{Kp e^{\frac{\epsilon_m^*}{kT}} - 1 + \left(1 + Kp e^{\frac{\epsilon_m^*}{kT}}\right) \exp(4pK_s' t)} \quad (19)$$

For comparison we prepared analogous figures for the equilibrium dominated systems using Eqs. (18) and (19). It is clearly seen that the results obtained by using the equilibrium dominated version of

the SRT kinetic equation are much different than those obtained for volume and solid dominated systems. The function $\epsilon_c^{(E)}$ has different shape and decreases much faster than the functions $\epsilon_c^{(V)}$ and $\epsilon_c^{(S)}$.

It is evident that the assumption of an equilibrium dominated system leads to the Elovich behavior. We can see in Fig. 3 that the kinetic isotherm plotted in the linear-logarithmic coordinates is linear for several magnitudes of time. Deviations from Elovich behavior for long times are due to the simultaneous desorption, which the classical Elovich Eq. (15) does not account for.

One can raise the question why the volume and solid dominated versions of the SRT kinetic equation do not lead to the Elovich equation. One possible answer is that the adsorption kinetics experiments have commonly been carried out under quasi-equilibrium conditions, so the correct version of the SRT equation is just the equilibrium dominated one. There is a little experimental evidence for such behavior of kinetic curves as predicted by the volume and solid dominated systems, i.e., linear dependence of coverage versus time [Low, 1960]. Moreover, in one of our recent publications [Panczyk and Rudzinski, 2003], we have shown that the volume and solid dominated versions of the SRT kinetic equation may even lead to concave shapes of kinetic isotherms for the case of quasi-gaussian adsorption energy distribution. Such shapes of kinetic isotherms are scarce in the reported literature data.

So, one may not exclude the fact that such strange behavior of the volume and solid dominated systems may have its source in ap-

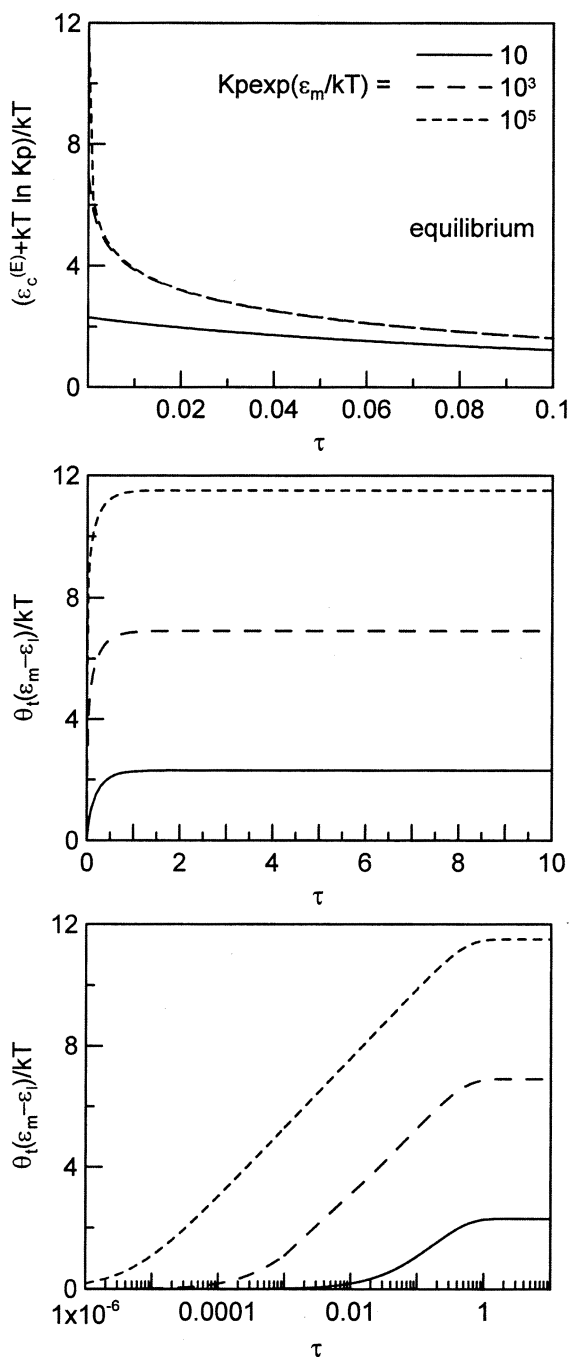


Fig. 3. The function $\epsilon_c^{(E)}$ for a few values of the parameter $Kp \exp(\epsilon_m/kT)$ and the corresponding kinetic isotherms of adsorption for the equilibrium dominated system.

plication of the Condensation Approximation to generalize the SRT equation for the case of energetically heterogeneous surfaces. It seems therefore necessary to carry out further theoretical studies on the generalization of the SRT equation for the case of energetically heterogeneous surfaces.

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