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Statistical fractal adsorption isotherms, linear energy relations, and power-law trapping-time distributions in porous media

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Drazer and Zanette [Phys. Rev. E **60**, 5858 (1999)] have reported on interesting experiments which show that trapping-time distributions in porous media obey a scaling law of the negative power-law type. Unfortunately, their theoretical interpretation of the experimental data has physical and mathematical inconsistencies and errors. Drazer and Zanette assume the existence of a distribution of local adsorption isotherms for which the random parameter is not a thermodynamic function, but a kinetic parameter, the trapping time. Moreover, they mistakenly identify the reciprocal value of a rate coefficient with the instantaneous (fluctuating) value of the trapping time. Their approach leads to mathematically inconsistent probability densities for the trapping times, which they find to be non-normalizable. We suggest a different theory, which is physically and mathematically consistent. We start with the classical patch approximation, which assumes the existence of a distribution of adsorption heats, and introduce two linear energy relationships between the activation energies of the adsorption and desorption processes and the adsorption heat. If the distribution of the adsorption heat obeys the exponential law of Zeldovich and Roghinsky, then both the adsorption isotherm and the probability density of trapping times can be evaluated analytically in terms of the incomplete beta and gamma functions, respectively. Our probability density of the trapping times is mathematically consistent; that is, it is nonnegative and normalized to unity. For large times it has a long tail which obeys a scaling law of the negative power-law type, which is consistent with the experimental data of Drazer and Zanette. By using their data we can evaluate the numerical values of the proportionality coefficients in the linear energy relations. The theory suggests that experimental study of the temperature dependence of the fractal exponents helps to elucidate the mechanism of the adsorption-desorption process.

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I. INTRODUCTION

The study of fractal time and of its connections with dispersive diffusion was initiated by Montroll and co-workers in the early 1970s [1,2]. Recently, this subject has become an important topic of applied statistical physics, with applications in various branches of science and technology, ranging from population dynamics and vital statistics to applied chemical kinetics and radiochemistry and to reliability analysis and economics [3,4].

In an interesting paper, Drazer and Zanette [5] have shown that the solute transport in desorption experiments in porous media, made of packings of activated carbon grains, follows the dispersive mechanism suggested by Montroll and co-workers, which corresponds to power-law trapping-time distributions. They have used nonconsolidated packings of relatively uniform, spherical, activated carbon grains obtained from apricot pits, with an average radius of $d=(0.13\pm 0.01)$ cm. The carbon grains were packed in a 30-cm-high, 2.54-cm-inner-diameter cylinder. In the experiments, the porous medium is initially filled up with aqueous 0.1 M NaI solution tagged with ^{131}I. The authors have performed measurements of tracer adsorption and dispersion, in which a stepwise variation of the concentration of ^{131}I is induced at time $t=0$ and kept constant thereafter. Two different types of experiments with a total constant flow rate were carried out by using different displacing fluids. In the first set of experiments, the system was flushed with an untagged NaI solution having the same concentration as the initial, labeled, solution (exchange experiments), whereas in the second set of experiments the untagged NaI solution was replaced by distilled water (desorption experiments). The results of the exchange experiments show that the replacement of the radioactive isotope ^{131}I obeys a classical adsorption-desorption and dispersion mechanism commonly encountered in chemical engineering. In this case the observed concentration profiles can be reproduced theoretically by using a classical reaction-convection-diffusion equation. The time dependence of the concentration of ^{131}I is described by a set of kinetic curves, which decay very fast to zero. In the case of desorption experiments, the concentration profiles ^{131}I also decrease to zero for large times, but this decrease is much slower than in the case of exchange experiments. In the case of desorption for large times, the concentration profiles converge towards a long-time tail of the negative power-law type, $C(t)\sim t^{-\mu}$, $t\gg 0$, characterized by a fractal exponent $\mu=0.63$. Such long tails cannot be explained by assuming a classical reaction-diffusion mechanism. The experimental results of the authors suggest that the displacement of the radioactive isotope ^{131}I involves a very slow, dispersive (Montroll and co-workers) diffusion process. The qualitative physical picture suggested by the authors is the following: the motion of an atom of the radioactive isotope along the column can be represented by a hopping mechanism involving a succession of desorption and readsoption processes, which is basically a random walk in continuous time (CTRW [1–4]). According to Montroll and co-workers' theory of dispersive diffusion, such a continuous time random walk may lead to concentration profiles with long-time tails of the negative power-law type if the probability density of the trapping time of the radioactive isotope in the adsorbed state on the surface has a long time tail [1–4].

Drazer and Zanette have tried to give a theoretical interpretation of their experimental results, but unfortunately their treatment contains a number of errors and confusions. In order to compute the probability density of the trapping time, they assume that at any position in their apparatus, there is a local equilibrium between the solution and the surface of the carbon grains and that the carbon surface is heterogeneous. They invoke the homottatic patch approximation in heterogeneous catalysis [6] according to which the overall adsorption isotherm is made up of a contribution of local Langmuir adsorption isotherms

$$\theta_{\mathrm{local}}=\frac{K_{\mathrm{local}}^{\mathrm{eq}}C}{1+K_{\mathrm{local}}^{\mathrm{eq}}C}, \tag{1}$$

where θ_{local} is the local coverage of the surface, C is the local concentration of the chemical in the solution, and

$$K_{\mathrm{local}}^{\mathrm{eq}}(T)=k_{\mathrm{local}}^{+}/k_{\mathrm{local}}^{-}=K_{\mathrm{local}}^{\mathrm{eq}}(\infty)\exp\left[-\frac{\Delta H}{k_BT}\right] \tag{2}$$

is the local equilibrium constant of the adsorption process,

$$k_{\mathrm{local}}^{\pm}(T)=k_{\mathrm{local}}^{\pm}(\infty)\exp\left[-\frac{E^{\pm}}{k_BT}\right] \tag{3}$$

are local adsorption and desorption rates, respectively, $E^{\pm}$ are activation energies,

$$\Delta H=E^{+}-E^{-}=-\mathcal{E} \tag{4}$$

is the local change of the enthalpy during the adsorption process, $\mathcal{E}$ is the adsorption heat, k_B is Boltzmann's constant, and T is the temperature of the system. Drazer and Zanette mention that, according to the patch approximation in heterogeneous catalysis, different patches of the surface are characterized by different adsorption enthalpies and that their statistical distribution can be described in terms of a probability density

$$p(\mathcal{E})d\mathcal{E} \quad \text{with} \quad \int p(\mathcal{E})d\mathcal{E}=1; \tag{5}$$

the total adsorption isotherm can be expressed as an average of the local isotherm (1) with respect to the adsorption heat:

$$\theta=\int \theta_{\mathrm{local}}(\mathcal{E})p(\mathcal{E})d\mathcal{E}=\int \frac{K_{\mathrm{local}}^{\mathrm{eq}}(\mathcal{E},T)C}{1+K_{\mathrm{local}}^{\mathrm{eq}}(\mathcal{E},T)C}p(\mathcal{E})d\mathcal{E}. \tag{6}$$

So far, there is no problem. At this point, however, they make the conjecture that the local equilibrium constant is proportional to the trapping time τ of a molecule on the surface:

$$\tau=\frac{1}{w}K_{\mathrm{local}}^{\mathrm{eq}}(\mathcal{E},T), \tag{7}$$

where w is a proportionality factor. By using this conjecture, which is open to criticism, they express the overall adsorption isotherm (6) in the form

$$\theta=\int \theta_{\mathrm{local}}(\tau)\varphi(\tau)d\tau=\int \frac{w\tau C}{1+w\tau C}\varphi(\tau)d\tau, \tag{8}$$

where

$$\varphi(\tau)d\tau \quad \text{with} \quad \int \varphi(\tau)d\tau=1 \tag{9}$$

is the probability that the trapping time on the surface has a value between τ and $\tau+d\tau$.

For the experimental system studied, the overall adsorption isotherm obeys the Freundlich power law

$$\theta=\kappa C^{\alpha}, \quad 1>\alpha>0. \tag{10}$$

By combining Eqs. (8) and (9), Drazer and Zanette obtain an integral equation in $\varphi(\tau)$ which can be solved by using the Stieltjes transform, resulting in

$$\varphi(\tau)=\mathcal{J}^{\alpha}/\tau^{1+\alpha}. \tag{11}$$

Equation (11) is consistent with the experimental data. The probability density (11) has a singularity for $\tau=0$ and because of this singularity the integral $\int_0^{\infty}\varphi(\tau)d\tau=\infty$; that is, the probability density of the trapping time is not normalizable, a result which is mathematically incorrect. This divergence is due to the fact that the Freundlich isotherm (10) is not correct for large concentrations. Although in the reported experiments the concentrations are in the range for which the Freundlich isotherm is valid, the theoretical approach based on the assumption that the power law (11) holds for any values of the trapping time, from zero to infinity, is physically and mathematically inconsistent. We emphasize that for consistency with experimental data it is enough if only the tail of the probability density $\varphi(\tau)$ of the trapping times has the scaling form (11). This is due to the fact that, according to the theory of Montroll and co-workers, the properties of dispersive diffusion are determined by the Laplace transform of the probability density of the trapping time, $\overline{\varphi(s)}=\int_0^{\infty}\varphi(\tau)\exp(-s\tau)d\tau$, for small values of the Laplace variable, $s\to 0$. The form of the Laplace transform $\overline{\varphi(s)}$ of the trapping time probability density $\varphi(\tau)$ depends only on the shape of the tail of the function $\varphi(\tau)$ as $\tau\to\infty$ and is insensitive with respect to the details of the function $\varphi(\tau)$ for small trapping times. We conclude that a physically consistent theory should come up with a probability density $\varphi(\tau)$ obeying the scaling law (11) for large trapping times $\tau\to\infty$, but which, unlike Eq. (11), has a cumulative distribution function $\Phi(\tau)=\int_0^{\tau}\varphi(\tau)d\tau$ which is not singular for $\tau=0$—that is, $\lim\Phi(\tau)=$ finite as $\tau\to 0$—ensuring that the probability density $\varphi(\tau)$ is properly normalized to unity.

The unproven conjecture (7) generates serious inconsistencies in the theory, due to the fact that it assumes the existence of a deterministic relationship between two random variables, the trapping time and the local adsorption heat. In general, within the framework of the homottatic patch approximation used by Drazer and Zanette, there is no deterministic relationship between the trapping time and the local adsorption heat and the relation between these two random variables is not deterministic. The conjecture (7) is generated by a confusion between the reciprocal value of the adsorption rate, $1/k_{\mathrm{local}}^{-}$, and the trapping time. Drazer and Zanette assume, without proof, that $1/k_{\mathrm{local}}^{-}$ is equal to a random (fluctuating) value of the trapping time, corresponding to the adsorption heat $\mathcal{E}$. We are going to show that this assumption is not correct and that, under suitable circumstances, at local equilibrium, $1/k_{\mathrm{local}}^{-}$, can be interpreted as the *conditional average trapping time* of a local equilibrium state characterized by the adsorption heat $\mathcal{E}$.

The purpose of this article is to develop a physically consistent theory for explaining the experimental results of Drazer and Zanette. We shall show that the conjecture (7) is not appropriate and, moreover, that it is not necessary for explaining the experimental data. An adequate theoretical description of their data can be given by combining the classical homottatic patch approximation with the theory of lifetime distributions of reaction intermediates in complex chemical systems [7]. The structure of the paper is the following. In Sec. II we present the main assumptions of our approach. In Sec. III we study the equilibrium properties of the system, expressed in terms of the overall adsorption isotherm. Section IV deals with the evaluation of the trapping time distributions. Finally, in Sec. V we compare our theory with the Drazer-Zanette approach.

II. FORMULATION OF THE PROBLEM

In our approach the adsorption equilibrium is described by the homottatic patch approximation [6], and thus we assume the validity of Eqs. (1)–(6) of Sec. I. In addition, we assume that the activation energies $E^{\pm}$ of the adsorption-desorption processes and the local adsorption heat $\mathcal{E}=-\Delta H$ are related to each other by means of the linear relations

$$E_{\pm}=E_{\pm}^{0}+\beta_{\pm}\Delta H=E_{\pm}^{0}-\beta_{\pm}\mathcal{E}, \tag{12}$$

where $\beta_{\pm}$ are proportionality (scaling) coefficients. The existence of the linear relationships (12) for adsorption kinetics has been well documented in the literature of heterogeneous catalysis, both experimentally and theoretically [8]. In the literature of chemical kinetics, the relations (12) are referred to as Polanyi relations or ‘‘linear free energy relations’’ even though they involve the adsorption enthalpy rather than the Gibbs or Helmholtz free energy. They are equivalent to linear free energy relations only if the entropy factors of the adsorption-desorption process, both thermodynamic and kinetic, are the same for all active sites on the surface [8]. From Eqs. (4) and (12), it follows that the scaling coefficients $\beta_{\pm}$ are related to each other by means of the relationship

$$\beta_{+}=\beta_{-}+1. \tag{13}$$

An important consequence of the linear energy relations (12) is that the rate coefficients k_{local}^{+} are deterministic functions of the adsorption heat $\mathcal{E}=-\Delta H$:

$$k_{\mathrm{local}}^{\pm}(T)=k_{\mathrm{local}}^{\pm}(\infty)\{\exp[\mathcal{E}/k_BT]\}^{\beta_{\pm}}, \tag{14}$$

and thus, both for thermodynamic and kinetic variables, the global averages can be expressed in terms of the probability density $p(\mathcal{E})$ of the adsorption heat.

In order to describe the random properties of the trapping times, we use the theory of lifetime distributions of active intermediates in complex chemical systems [7]. We formally represent the adsorption-desorption process as a chemical reaction

$$X+Y(\mathcal{E})\rightleftarrows Z(\mathcal{E}) \tag{15}$$

and denote by $[X]=C$ the concentration of chemical in the solution, by $[Y(\mathcal{E})]=y(\mathcal{E})d\mathcal{E}$ the surface concentration of free sites with an adsorption heat between $\mathcal{E}$ and $\mathcal{E}+d\mathcal{E}$, and by $[Z(\mathcal{E})]=z(\mathcal{E})d\mathcal{E}$ the corresponding surface concentration of occupied sites. We also introduce a joint density function for the adsorption heat and the trapping time:

$$\eta_z(\tau,\mathcal{E})d\mathcal{E}\,d\tau \quad \text{with} \quad z(\mathcal{E})d\mathcal{E}=d\mathcal{E}\int \eta_z(\tau,\mathcal{E})d\tau. \tag{16}$$

Here $\eta_z(\tau,\mathcal{E})d\mathcal{E}\,d\tau$ is the surface concentration of occupied sites with an adsorption heat between $\mathcal{E}$ and $\mathcal{E}+d\mathcal{E}$ and which has trapped a molecule for a time interval between τ and $\tau+d\tau$. The density function can be computed from the balance equations

$$\left(\frac{\partial}{\partial t}+\frac{\partial}{\partial \tau}\right)\eta_z(\tau,\mathcal{E})d\mathcal{E}\,d\tau=-\eta_z(\tau,\mathcal{E})k_{\mathrm{local}}^{-}(\infty)\times\{\exp[\mathcal{E}/k_BT]\}^{\beta_{+}-1}, \tag{17}$$

$$\eta_z(\tau=0,\mathcal{E})=Cy(\mathcal{E})k_{+}^{0}\{\exp[-\mathcal{E}/k_BT]\}^{\beta_{+}} \tag{18}$$

In terms of the density function $\eta_z(\tau,\mathcal{E})d\mathcal{E}\,d\tau$, we can compute the conditional probability density

$$\varphi(\tau|\mathcal{E})=\frac{\eta_z(\tau,\mathcal{E})}{\int \eta_z(\tau,\mathcal{E})d\tau} \quad \text{with} \quad \int \varphi(\tau|\mathcal{E})d\tau=1 \tag{19}$$

of the trapping time corresponding to a given value of the adsorption heat. Finally, the unconditional probability density of the trapping times can be evaluated by averaging over all possible values of the adsorption heat:

$$\varphi(\tau)=\int \varphi(\tau|\mathcal{E})p(\mathcal{E})d\mathcal{E} \quad \text{with} \quad \int \varphi(\tau)d\tau=1. \tag{20}$$

By using our approach it is possible to compute the probability density of the trapping times, $\varphi(\tau)$, in terms of the probability density $p(\mathcal{E})$ of the adsorption heat. In order to compare our approach with the experimental data of Drazer and Zanette, we have to assume a model for this probability density. In the following we use the Zeldovich-Roginskii model [9], for which the adsorption heat can take any positive value between zero and infinity, and the probability density $p(\mathcal{E})$ is exponential:

$$p(\mathcal{E})=(k_BT^*)^{-1}\exp[-\mathcal{E}/(k_BT^*)]$$

$$\text{with}\quad\int_0^\infty p(\mathcal{E})d\mathcal{E}=1,\quad T^*>T. \tag{21}$$

The physical meaning of the Zeldovich-Roginksii model has been discussed in detail in the literature [9,10]: it corresponds to a canonical distribution ''frozen'' at a temperature $T^*>T$, where T is the current temperature of the system. The value of the characteristic temperature $T^*>T$ provides information about the history of processing the surface.

III. FRACTAL ADSORPTION EQUILIBRIUM AND GENERALIZED FREUNDLICH ISOTHERM

We begin the analysis of our model by studying the adsorption equilibrium. At equilibrium, the adsorption rate equals the desorption rate, resulting in

$$Cy(\mathcal{E})k^{+}_{\text{local}}(\infty)\{\exp[\mathcal{E}/k_BT]\}^{\beta_+}$$

$$=z(\mathcal{E})k^{-}_{\text{local}}(\infty)\{\exp[\mathcal{E}/k_BT]\}^{\beta_+-1}. \tag{22}$$

In addition, the total number of sites, occupied and free, is conserved, and thus we have the balance equation

$$y(\mathcal{E})+z(\mathcal{E})=u(\mathcal{E}), \tag{23}$$

where $u(\mathcal{E})d\mathcal{E}$ is the total number of sites, free and occupied, with an adsorption heat between $\mathcal{E}$ and $\mathcal{E}+d\mathcal{E}$. By solving Eqs. (22) and (23), we come to

$$z(\mathcal{E})=u(\mathcal{E})\,\frac{CK^{\text{eq}}_{\text{local}}(\infty)\exp[\mathcal{E}/(k_BT)]}{1+CK^{\text{eq}}_{\text{local}}(\infty)\exp[\mathcal{E}/(k_BT)]}, \tag{24}$$

where the local equilibrium constants $K^{\text{eq}}_{\text{local}}(T)$ and $K^{\text{eq}}_{\text{local}}(\infty)$ for temperature T are expressed as ratios of the corresponding forward and backward rate coefficients:

$$K^{\text{eq}}_{\text{local}}(T)=k^{+}_{\text{local}}(T)/k^{-}_{\text{local}}(T)=K^{\text{eq}}_{\text{local}}(\infty)\exp[-\Delta H/(k_BT)], \tag{25}$$

$$K^{\text{eq}}_{\text{local}}(\infty)=k^{+}_{\text{local}}(\infty)/k^{-}_{\text{local}}(\infty). \tag{26}$$

By integrating Eq. (24) over all possible values of the adsorption heat, we recover Eq. (6) for the overall adsorption isotherm:

$$\theta=\frac{Z(C)}{U}=\int\frac{CK^{\text{eq}}_{\text{local}}(\infty)\exp[-\mathcal{E}/(k_BT)]}{1+CK^{\text{eq}}_{\text{local}}(\infty)\exp[-\mathcal{E}/(k_BT)]}p(\mathcal{E})d\mathcal{E}, \tag{27}$$

where

$$Z(C)=\int z(\mathcal{E})d\mathcal{E}\,U=\int u(\mathcal{E})d\mathcal{E} \tag{28}$$

is the total surface concentration of occupied sites and

$$U=\int u(\mathcal{E})d\mathcal{E} \tag{29}$$

is the total surface concentration of active sites, free and occupied. In Eq. (27) the probability density $p(\mathcal{E})d\mathcal{E}$ is expressed as a ratio between the surface concentration $u(\mathcal{E})d\mathcal{E}$ of active sites with the adsorption heat between $\mathcal{E}$ and $\mathcal{E}+d\mathcal{E}$, and the total surface concentration U of active sites:

$$p(\mathcal{E})d\mathcal{E}=u(\mathcal{E})d\mathcal{E}/U. \tag{30}$$

We insert the Zeldovich-Roginskii distribution (21) into Eq. (27) and evaluate the integral over the adsorption heat $\mathcal{E}$. After a number of transformations we obtain

$$\begin{aligned}\theta&=\alpha(CK^{\text{eq}}_{\text{local}}(\infty))^{\alpha}\left\{B(1-\alpha,\alpha)\right.\\&\quad\left.-B\left(1-\alpha,\alpha;\frac{CK^{\text{eq}}_{\text{local}}(\infty)}{1+CK^{\text{eq}}_{\text{local}}(\infty)}\right)\right\}\\&=(CK^{\text{eq}}_{\text{local}}(\infty))^{\alpha}\frac{\pi\alpha}{\sin(\pi\alpha)}-\alpha(CK^{\text{eq}}_{\text{local}}(\infty))^{\alpha}\\&\quad\times B\left(1-\alpha,\alpha;\frac{CK^{\text{eq}}_{\text{local}}(\infty)}{1+CK^{\text{eq}}_{\text{local}}(\infty)}\right),\end{aligned} \tag{31}$$

where

$$B(p,q)=\int_0^1 x^{q-1}(1-x)^{q-1}dx,\quad q,p>0, \tag{32}$$

$$B(p,q;x)=\int_0^x x^{q-1}(1-x)^{q-1}dx,\quad q,p>0,\quad x\geqslant 0, \tag{33}$$

are the complete and the incomplete beta functions, respectively, and

$$\alpha=T/T^*,\quad 1>\alpha>0, \tag{34}$$

is a scaling exponent between zero and unity.

From Eq. (31) we notice that, in the limit of very small concentrations in solution, $C\to 0$, we recover the Freundlich isotherm [10]

$$\theta\sim(CK^{\text{eq}}_{\text{local}}(\infty))^{\alpha}\frac{\pi\alpha}{\sin(\pi\alpha)}\quad\text{as}\quad C\to 0. \tag{35}$$

In the other limit of large concentrations, the adsorption isotherm (31) tends towards a constant value:

$$\theta\to 1\quad\text{as}\quad C\to\infty. \tag{36}$$

IV. TRAPPING-TIME DISTRIBUTIONS

At local equilibrium the time derivative in Eq. (17) is equal to zero and the joint density function $\eta_Z(\tau,\mathcal{E})$ can be easily evaluated. By integrating Eq. (17) with the initial condition (18), we obtain

$$\begin{aligned}\eta_Z(\tau,\mathcal{E})&=Cy(\mathcal{E})k^{+}_{\text{local}}(\infty)\exp[\beta_+\mathcal{E}/k_BT]\\&\quad\times\exp\{-\tau k^{-}_{\text{local}}(\infty)\exp[(\beta_+-1)\mathcal{E}/(k_BT)]\}\\&=u(\mathcal{E})\,\frac{CK^{\text{eq}}_{\text{local}}(\infty)\exp[\beta_+\mathcal{E}/(k_BT)]}{1+CK^{\text{eq}}_{\text{local}}(\infty)\exp[\mathcal{E}/(k_BT)]}k^{-}_{\text{local}}(\infty)\\&\quad\times\exp\{-\tau k^{-}_{\text{local}}(\infty)\exp[(\beta_+-1)\mathcal{E}/(k_BT)]\}.\end{aligned} \tag{37}$$

By combining Eqs. (19) and (38), we can compute the conditional probability density $\varphi(\tau|\mathcal{E})$ of the trapping times corresponding to a given value of the adsorption heat:

$$\varphi(\tau|\mathcal{E})=k_{\text{local}}^{-}(\infty)\exp[(\beta_{+}-1)\mathcal{E}/(k_BT)]\times\exp\{-\tau k_{\text{local}}^{-}(\infty)\exp[(\beta_{+}-1)\mathcal{E}/(k_BT)]\}. \tag{38}$$

By using Eqs. (14), Eq. (37) can be rewritten in a simpler form

$$\varphi(\tau|\mathcal{E})=k_{\text{local}}^{-}(\mathcal{E},T)\exp\{-\tau k_{\text{local}}^{-}(\mathcal{E},T)\}. \tag{39}$$

We notice that the conditional probability density of the trapping times is an exponential with a characteristic decay rate $k_{\text{local}}^{-}(\mathcal{E},T)$. In particular, the conditional average value of the trapping times is equal to the reciprocal value of the decay rate, $k_{\text{local}}^{-}(\mathcal{E},T)$:

$$\langle\tau(\mathcal{E})\rangle_{|\varepsilon}=\int_0^\infty\tau\varphi(\tau|\mathcal{E})d\tau=1/k_{\text{local}}^{-}(\mathcal{E},T). \tag{40}$$

The unconditional probability density of the trapping times can be evaluated from Eqs. (20), (21), and (38). After some algebra we come to

$$\varphi(\tau)=\alpha\tau^{-[(1+\alpha)/(1-\beta_{+})]}[k_{\text{local}}^{-}(\infty)]^{-[(\alpha+\beta_{+})/(1-\beta_{+})]}\times\gamma\left(\frac{1+\alpha}{1-\beta_{+}},\tau k_{\text{local}}^{-}(\infty)\right), \tag{41}$$

where

$$\gamma(a,x)=\int_0^x t^{a-1}\exp(-t)dt\quad\text{with}\quad a>0,\quad x\geqslant 0, \tag{42}$$

is the incomplete γ function. In Eq. (41), for physical consistency we have to assume that

$$\frac{1-\alpha}{2}>\beta_{+}>-\alpha. \tag{43}$$

These restrictions must be introduced in order to ensure the non-negativity and normalization to unity of the probability density of trapping times. We shall see later that restrictions (43) are fulfilled by the experimental data reported by Drazer and Zanette. Unlike the law (11) for $\varphi(\tau)$ derived by Drazer and Zanette, the function $\varphi(\tau)$ given by Eq. (41) is a properly defined probability density; that is, it is non-negative and normalized to unity.

The probability density (41) for the trapping time has the same type of asymptotic behavior as the improper probability density (11) derived by Drazer and Zanette. We have

$$\varphi(\tau)\sim\alpha(k_{\text{local}}^{-}(\infty))^{-[(\alpha+\beta_{+})/(1-\beta_{+})]}\times\Gamma\left(\frac{1+\alpha}{1-\beta_{+}}\right)\tau^{-[(1+\alpha)/(1-\beta_{+})]}=\frac{\mathcal{J}^{\alpha_{\text{eff}}}}{\tau^{1+\alpha_{\text{eff}}}}\quad\text{as}\quad\tau\to\infty, \tag{44}$$

where the characteristic time $\mathcal{J}$ and the effective scaling exponent α_{eff} are given by

$$\mathcal{J}=\frac{1}{k_{\text{local}}^{-}(\infty)}\left[\alpha\Gamma\left(\frac{1+\alpha}{1-\beta_{+}}\right)\right]^{(1-\beta_{+})/(\alpha+\beta_{+})}, \tag{45}$$

$$\alpha_{\text{eff}}=\frac{\alpha+\beta_{+}}{1-\beta_{+}}\quad\text{with}\quad 1>\alpha_{\text{eff}}>0 \tag{46}$$

and

$$\Gamma(a)=\int_0^\infty t^{a-1}\exp(-t)dt\quad\text{with}\quad a>0 \tag{47}$$

is the complete gamma function. All positive moments of order bigger than α_{eff} are infinite:

$$\langle\tau^m\rangle=\infty\quad\text{for}\quad m>\alpha_{\text{eff}}. \tag{48}$$

This is a typical feature for a statistical fractal probability density [2,4].

In conclusion, in this section we have shown that, by combining the classical homottatic approximation with the theory of lifetime distributions of reaction intermediates in complex chemical systems, it is possible to derive a distribution of trapping times with a long tail, which is compatible with the experimental data of Drazer and Zanette and is properly normalized to unity. The proportionality law (7) suggested in [5] is neither necessary nor appropriate for the development of the theory.

V. COMPARISON WITH THE DRAZER-ZANETTE APPROACH: DISCUSSION

We start out the comparison between our theory and the Drazer-Zanette approach by searching for the possible existence of a proportionality law similar to Eq. (7). By using the linear free energy relations (12), we can express the local desorption rate $k_{\text{local}}^{-}(\mathcal{E})$ in terms of the equilibrium constant $K_{\text{local}}^{\text{eq}}(\mathcal{E},T)$. We have

$$k_{\text{local}}^{-}(\mathcal{E},T)=k_{\text{local}}^{-}(\infty)\left\{\frac{K_{\text{local}}^{\text{eq}}(\mathcal{E},T)}{K_{\text{local}}^{\text{eq}}(\infty)}\right\}^{\beta_{+}-1}. \tag{49}$$

By combining Eqs. (40) and (49), we come to

$$\langle\tau(\mathcal{E})\rangle_{|\varepsilon}=\frac{1}{w}[K_{\text{local}}^{\text{eq}}(\mathcal{E},T)]^{1-\beta_{+}}, \tag{50}$$

where

$$w=k_{\text{local}}^{-}(\infty)[K_{\text{local}}^{\text{eq}}(\infty)]^{1-\beta_{+}}. \tag{51}$$

Equation (50) has a similar structure as Eq. (7) postulated by Drazer and Zanette. However, Eqs. (7) and (50) are very different: Equation (7) is a deterministic relation between two random quantities, the fluctuating values of the adsorption heat and the trapping time, whereas Eq. (50) is a relation between the conditional average of the trapping time corresponding to a given value (realization) of the adsorption heat and the value of the adsorption heat. The differences between the two approaches is obvious in the corresponding expressions of the joint probability distribution of the trapping time and adsorption heat:

$\psi(\tau,\mathcal{E})\,d\tau\,d\mathcal{E}$ with the normalization condition

$$\int_0^\infty \int_0^\infty \psi(\tau,\mathcal{E})\,d\tau\,d\mathcal{E}=1. \tag{52}$$

Within the framework of the homottatic patch approximation, the correct expression of this joint probability is given by

$$\psi(\tau,\mathcal{E})\,d\tau\,d\mathcal{E}=\varphi(\tau|\mathcal{E})\,d\tau\,p(\mathcal{E})\,d\mathcal{E}$$
$$=k_{\text{local}}^{-}(\mathcal{E},T)\exp\{-\tau k_{\text{local}}^{-}(\mathcal{E},T)\}p(\mathcal{E})\,d\tau\,d\mathcal{E}. \tag{53}$$

As expected, the adsorption heat, which is a thermodynamic function, is independent of the trapping time, which is a kinetic variable. The opposite is, however, not true: the trapping time depends on the value of the adsorption heat, and the relation between these two variables is not deterministic, but random, and is expressed by the conditional probability density (39).

The Drazer-Zanette conjecture (7) implies that the conditional probability density $\varphi(\tau|\mathcal{E})$ is given by a δ function

$$\varphi(\tau|\mathcal{E})=\delta\left[\tau-\frac{1}{w}K_{\text{local}}^{\text{eq}}(\mathcal{E},T)\right],$$

which corresponds to the following joint probability density:

$$\psi(\tau,\mathcal{E})\,d\tau\,d\mathcal{E}=\delta\left[\tau-\frac{1}{w}K_{\text{local}}^{\text{eq}}(\mathcal{E},T)\right]p(\mathcal{E})\,d\tau\,d\mathcal{E}. \tag{54}$$

Equation (54) is not compatible with Eq. (53) as well as with Eq. (39) derived from the homotattic patchwise approximation.

Another difference between the two theories refers to the scaling conditions resulting from the computations. Our theory depends on two independent scaling exponents, the fractal exponent α entering the Freundlich adsorption isotherm (35) and one of the scaling parameters β_+ or β_- entering the linear free energy relations (12). The fractal exponent α_{eff}, which determines the shape of the tail of the trapping-time distribution, is a combination of these two scaling exponents, given by Eq. (46). Drazer and Zanette have not assumed the existence of linear energy relationships, and because of that, their theory has only one scaling exponent which determines both the shape of the Freundlich isotherm and the tail of the trapping-time distribution.

The desorption experiments presented in [5] show that

$$\alpha=\alpha_{\text{eff}}=0.63. \tag{55}$$

By applying Eqs. (13) and (46), we can evaluate the numerical values of the scaling exponents $\beta_\pm$ entering the linear energy relations (12),

$$\beta_+=0, \quad \beta_-=-1 \tag{56}$$

and, thus

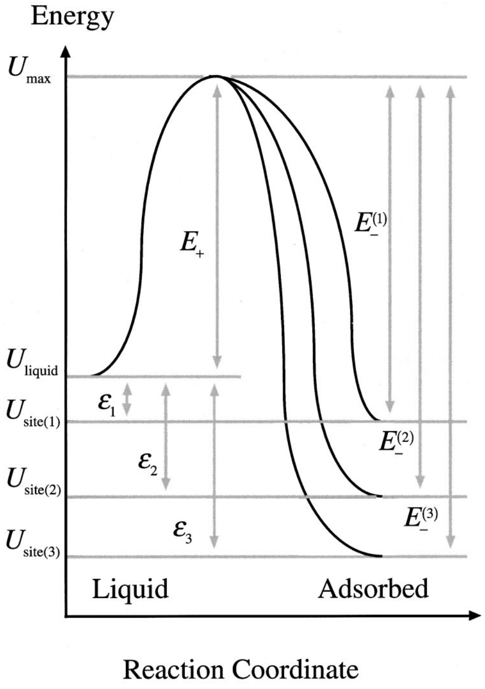

FIG. 1. Schematic representation of the activation energy profiles for the adsorption-desorption process studied in the experiments of Drazer and Zanette [5]. The different activation energy profiles correspond to adsorption sites characterized by different adsorption heats. All energy profiles start from the same value U_{liquid}, which corresponds to the liquid phase, increase up to the same maximum value U_{max}, and then decrease to various final values $U_{\text{site(1)}},U_{\text{site(2)}},U_{\text{site(3)}},\ldots,$ corresponding to surface sites characterized by various adsorption heats.

$$E_+=E_+^0=E_-^0=\text{const}, \tag{57}$$

$$E_-=E_-^0+\mathcal{E}. \tag{58}$$

It follows that the adsorption rate is constant for all adsorption sites, irrespective of the value of the adsorption heat. Only the desorption rate depends on the adsorption heat in a simple way: up to a constant additive factor, the activation energy of the desorption process is equal in magnitude to the adsorption heat of the site considered. The activation energy profiles for the adsorption-desorption process have the form represented schematically in Fig. 1, which represents different energy profiles for the adsorption-desorption process on sites characterized by different adsorption heats. All energy profiles start from the same energy value U_{liquid} corresponding to a molecule in the liquid phase and go up to the same maximum value U_{max}. The descending parts of the activation energy profiles are different for sites with different adsorption heats. The difference between the energy $U_{\text{site}(j)}$ corresponding to the surface site of type j and the characteristic energy U_{liquid} corresponding to a molecule in the liquid phase is equal to the variation of enthalpy during the adsorption process on the site j:

$$\Delta H_j=U_{\text{site}(j)}-U_{\text{liquid}}\leqslant 0. \tag{59}$$

The corresponding adsorption heat is equal to the variation of the enthalpy with a changed sign:

$$\mathcal{E}=-\Delta H_j=U_{\text{liquid}}-U_{\text{site}(j)}\geqslant 0. \tag{60}$$

The activation energy of the adsorption process is equal to the difference between the maximum value of the energy, U_{max} corresponding to the top of the various energy profiles and the characteristic energy U_{liquid} corresponding to a molecule in the liquid:

$$E_+=U_{\text{max}}-U_{\text{liquid}}. \tag{61}$$

Similarly, the activation energies $E_-^{(j)}$ of the desorption processes corresponding to the various sites of the surface are given by

$$E_-^{(j)}=U_{\text{max}}-U_{\text{site}(j)}. \tag{62}$$

We notice that, by combining Eqs. (60)–(62), we recover the linear energy relation (58), compatible with the experimental data of Drazer and Zanette. We have

$$\begin{aligned}E_-^{(j)}=U_{\text{max}}-U_{\text{site}(j)}&=(U_{\text{max}}-U_{\text{liquid}})+(U_{\text{liquid}}-U_{\text{site}(j)})\\&=E_-^0+\mathcal{E},\end{aligned} \tag{63}$$

where

$$E_-^0=U_{\text{max}}-U_{\text{liquid}}=E_+=E_+^0. \tag{64}$$

In the particular case described by Eqs. (56)–(58), the relation (50) between the conditional average $\langle\tau(\mathcal{E})\rangle_{|\varepsilon}$ of the trapping time attached to a given adsorption site and the local equilibrium constant $K_{\text{local}}^{\text{eq}}(\mathcal{E},T)$ for the adsorption process becomes a proportionality

$$\langle\tau(\mathcal{E})\rangle_{|\varepsilon}=\frac{1}{w}K_{\text{local}}^{\text{eq}}(\mathcal{E},T). \tag{65}$$

The similarity between Eqs. (7) and (65) is deceiving; as explained before, the terms on the left side of these equations have different meanings: in Eq. (7), τ is a random variable, the fluctuating value of the trapping time, whereas in Eq. (65) $\langle\tau(\mathcal{E})\rangle_{|\varepsilon}$ is the conditional average of the trapping time corresponding to a given value of the adsorption heat. The similar structure of Eqs. (7) and (65) is the main reason for which Drazer and Zanette managed to achieve a successful data fit by using a theoretical approach based on the conjecture (7).

Now we discuss an issue related to the temperature dependence of the fractal exponent α of the Freundlich adsorption isotherm. In our derivation we have used the original Zeldovich-Roginskii adsorption heat distribution [Eq. (21)]. This distribution leads to the consequence that the fractal exponent α is a linear function of the absolute temperature T of the system [Eq. (34)], a result which is consistent with the experimental data for many heterogeneous systems. However, more recent research reported in the literature shows that the exponent α can be a nonlinear function of temperature or even a constant. Theoretical treatments of these systems are based on a generalization of the Zeldovich-Roginskii distribution of the type [10]

$$p(\mathcal{E})=\frac{\alpha}{k_BT}\exp[-\alpha\mathcal{E}/(k_BT)] \quad \text{with} \quad \int_0^\infty p(\mathcal{E})d\mathcal{E}=1, \tag{66}$$

where now α is a positive scaling parameter. The theoretical justification of the distribution (66) is related to the constraint that the adsorption heat is a linear function of the coverage of the surface. This linear dependence of the adsorption heat on the coverage is encountered for many catalytic systems [10]. The theory developed in this article is also valid in the case of the generalized distribution (21), with the difference that now the temperature dependence of the scaling parameter α is generally unknown. In Ref. [5] there are no details concerning the temperature variation of the scaling parameter α. An experimental study of the temperature variation of the parameters α and α_{eff} would be of interest for elucidating the detailed mechanism of the adsorption process. In particular, a linear dependence of temperature would indicate that the distribution of adsorption heats is given by a frozen Maxwell-Boltzmann distribution of the Zeldovich-Roginskii type.

We finish our discussion by pointing out some limitations of our approach. Many of the equations derived in this article are independent of the minimum and maximum values of the adsorption heat $\mathcal{E}$. Although in the general formulation of our theory we have not specified the integration limits with respect to $\mathcal{E}$, in the final computations we have assumed that $\mathcal{E}$ can take any value between zero and infinity. Even though this range of variation of $\mathcal{E}$ is commonly used in the literature, it may be subject to criticism. A straightforward analysis of our equations shows that the modification of the lower integration limit from zero to an arbitrary (finite) positive or negative value does not change the shape of the tail of the probability density of the trapping times. The values of the scaling exponents computed in this article remain unchanged: only the expressions for some proportionality factors change. In the case of the upper integration limit, however, the situation is different. From the mathematical point of view, the long-time tails predicted by our theory are due to the fact that we have assumed that there is no finite upper limit for the values of the adsorption heat $\mathcal{E}$. However, a rigorous physical analysis shows that an infinite adsorption heat is a mathematical artifact. The maximum adsorption heat is associated with the closest possible packing configuration at a separation distance corresponding to the minimum of the van der Waals potential. Therefore, even though the maximum adsorption heat may be very large, it is, however, finite. In order that our theory be valid, it is enough that the maximum activation energy, although finite, be large enough, so that the beginning of the tail of the trapping time probability density obeys a scaling law of the negative power-law type. The finite value of the maximum adsorption heat results in a cutoff of the power-law portion of the tail. If such a cutoff exists outside the range of times experimentally available, it does not affect the predictions of our theory. We notice that such cutoff values for the ends of the tails of the fractal probability densities are commonly encountered in the literature (see, for example, Refs. [11–13]). Usually, perfect statistical fractals for which the self-similarity of the probability laws acts up to infinity do not exist: self-similarity is generally valid on a finite range of the random variables, limited by cutoff values.

Another simplification in our analysis is related to the graphical representation of the activation energy profiles in Fig. 1. The energy of a molecule in the liquid phase is a random variable, which obeys the laws of equilibrium statistical mechanics. In Eqs. (59)–(64), as well as in Fig. 1 we have neglected this energy distribution. This approximation, which is also commonly used in the literature, is justified by the fact that the energy distribution in the liquid phase is generally much narrower than the energy distribution on a heterogeneous surface.

VI. CONCLUSIONS

In this paper a theoretical approach has been introduced in order to interpret the Drazer-Zanette experiments on power-law trapping-time distributions in porous media. The model suggested here is based on the theory of lifetime distributions of active intermediates in complex chemical systems. The mathematical crux of the paper is the following. Drazer and Zanette assume that two random variables, the trapping time τ of a molecule on the surface and the local equilibrium constant $K_{\mathrm{local}}^{\mathrm{eq}}(\mathcal{E},T)$ for the adsorption on a site characterized by the adsorption heat $\mathcal{E}$, have a relationship of the form $\tau \sim K_{\mathrm{local}}^{\mathrm{eq}}(\mathcal{E},T)$, whereas the theory presented here proves that $\langle \tau(\mathcal{E})\rangle_{|\mathcal{E}} \sim [K_{\mathrm{local}}^{\mathrm{eq}}(\mathcal{E},T)]^{1-\beta_+}$, where $\langle \tau(\mathcal{E})\rangle_{|\mathcal{E}}$ is a conditional average and $K_{\mathrm{local}}^{\mathrm{eq}}(\mathcal{E},T)$ is the value of the equilibrium constant for a single realization of the process. The second relation is a consequence of a physically and mathematically consistent theory and explains the experimental data. The relation suggested by Drazer and Zanette, even though it ‘‘explains’’ the experimental results, leads to theoretical inconsistencies.

Although here we focus on the system studied experimentally by Drazer and Zanette, the results presented in this article have more general implications. The calculations presented in this paper can be easily extended to more complicated systems for which statistical fractal distributions are needed for the interpretation of experimental data—for example, to the case of protein-ligand interactions far from equilibrium [14].

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