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Reply to “Comment on ‘Computer Simulation of Static and Dynamic Properties During Transient Sorption of Fluids in Mesoporous Materials’”

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Valiullin et al. comment on my results on adsorption of fluids in independent cylindrical mesopores. In part, the content of their criticism is not quite clear. With respect to a key question under discussion, namely how or whether the relaxation time depends on the pressure, their comment suffers from an inconsistency that I will address first.

The first sentence by Valiullin et al. in the paragraph above their eq (1) reads:

“One of the main results presented is the dependence of relaxation time on external pressure along the adsorption and desorption isotherms as shown in Morgner’s Fig.4.”

Inspection of the upper panel in Figure 4 reveals clearly that my calculation leads to a pronounced dependence of the relaxation time as function of pressure. Therefore, one is somewhat puzzled to read at the end of point ii):

“Thus if Morgner’s proposal was true dynamic uptake curves would be independent of the pressure when plotted in the normalized form

$$\frac{f(t) - f(\infty)}{f(0) - f(\infty)} \text{ vs } t \quad (4)$$

In connection with their eq (3) $\Delta f(t) = \Delta f \exp[-t/\tau]$, where $\Delta f(t) = f(t) - f(\infty)$ and $\Delta f = f(0) - f(\infty)$, this statement appears to imply that I would propose the relaxation time to be independent of pressure. This is clearly the contrary of the results presented in my paper.

Thus, Valiullin et al. criticize me for an alleged statement that in fact appears to be their own.

Apart from this aspect their arguments deal with the following two aspects:

(1) They claim that their system is so different from the independent pore model that I have investigated that my simulation results have no bearing on the systems involving Vycor as mesoporous material. As their results on pressure jump experiments have a similar outcome as data by Wallacher et al.³ for porous silicon, they state that Vycor and porous silicon behave very similar to each other, but very different from the independent pore model.

(2) They put forward a concept of the relaxation time that in some respect indeed is different from mine. While I agree with their definition of relaxation time, I disagree with respect to their way of determining the value of the relaxation time. Valiullin et al. state “Even for systems exhibiting simple exponential decay (eq 1 for $\beta = 1$), the relaxation time is independent of the total amount of change in fractional filling. This is made amply clear by rewriting eq 1 (for $\beta = 1$) as $\Delta f(t) = \Delta f \exp[-t/\tau]$ (3) where $\Delta f(t) = f(t) - f(\infty)$ and $\Delta f = f(0) - f(\infty)$. A larger Δf only changes the magnitude of the relaxation function, not its time dependence”.

I start to discuss their concept of relaxation time.

Equation (1) by Valiullin et al. reads

$$\frac{f(t) - f(\infty)}{f(0) - f(\infty)} = \exp[-(t/\tau)^\beta]$$

with β ranging from 0.5 to 1. $\beta = 1$ is claimed by Valiullin et al. to describe adsorption of a fluid into simple independent pores.

For discussing this equation we write down the first derivative with respect to time

$$\frac{df(t)}{dt} \frac{1}{f(0) - f(\infty)} = -\left(\frac{t}{\tau}\right)^{\beta-1} \frac{\beta}{t} \exp[-(t/\tau)^\beta]$$

Making use of eq (1) by Valiullin et al. we get

$$\frac{df(t)}{dt} \frac{1}{f(0) - f(\infty)} = -\left(\frac{t}{\tau}\right)^{\beta-1} \frac{\beta}{t} \frac{f(t) - f(\infty)}{f(0) - f(\infty)}$$

As $f(0) - f(\infty) \neq 0$ we can reduce to

$$\frac{df(t)}{dt} = -\left(\frac{t}{\tau}\right)^{\beta-1} \frac{\beta}{t} (f(t) - f(\infty))$$

For simplicity, we specialize to $\beta = 1$ (we will see later that the key point of the following consideration is not affected by this setting)

$$\frac{df(t)}{dt} = -\frac{1}{\tau} (f(t) - f(\infty)) \quad (**)$$

From eq (**), we evaluate now an explicit expression for the relaxation time

$$\tau = \frac{(f(\infty) - f(t))}{\frac{df(t)}{dt}}$$

which turns out to be the amount $(f(\infty) - f(t))$ still to be transported at time t divided by the rate of transportation at time t . Equation 1 by Valiullin et al. as well as the eqs (*,**) contain definitions of the relaxation time. In the case of $\beta = 1$ the value of τ does not depend on time and one can evaluate τ by the expression at time $t = 0$

$$\tau = \frac{(f(\infty) - f(0))}{\frac{df(0)}{dt}}$$

I agree that these definitions are commonly used (in particular for $\beta = 1$), and thus they are appropriate in the present context.

The disagreement between Valiullin et al. and myself starts after putting up this definition. In my opinion, the key question to be addressed is by which quantity the speed of transportation $df(t)/dt$ is controlled.

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Valiullin et al. appear to claim that $df(0)/dt$ is proportional to the amount $(f(\infty) - f(0))$. This would lead to a relaxation time τ which is independent of the total amount to be transported $(f(\infty) - f(0))$, as stated by Valiullin et al. in the text above their eq 3: “Even for systems exhibiting simple exponential decay (eq 1 with $\beta = 1$), the relaxation time τ is independent of the total amount of change in fractional filling $\Delta f = f(0) - f(\infty)$ ”.

I dispute that this statement is generally valid. In general, the speed of transportation $df(t)/dt$ depends on the driving force. If we consider diffusional transport, the general equation is the ansatz by Onsager which reads at constant temperature T

$$J(t) = -\frac{L}{T} \left(\frac{d\mu}{dz}(t) \right)$$

where $J(t)$ denotes the current density, L is the diffusion coefficient, and $d\mu/dz$ is the gradient of the chemical potential, which is the driving force according to Onsager's ansatz.¹

The left side of Onsager's ansatz and the left side of eq (**), that is, $df(t)/dt$ and $J(t)$, are obviously proportional to each other, because the larger the current density the larger is the change rate of filling $f(t)$. In a pressure jump experiment, the pressure and, thus, the chemical potential of the reservoir is changed by a small amount Δp , or $\Delta\mu$. If these increments are chosen positive, the driving force $(d\mu/dz)(t)$ points from the reservoir to the pore.

Now, we discuss the same situation, but assuming, as Valiullin et al. do, that Fick's law can be applied

$$J(t) = -D \left(\frac{dc}{dz}(t) \right)$$

where $J(t)$ denotes the current density, dc/dz is the concentration gradient that is the driving force according to Fick's law, while D refers to the diffusion coefficient. The left side of Fick's law and the left side of eq (**), that is, $df(t)/dt$ and $J(t)$ must be proportional to each other as discussed before. If fluid is to diffuse from the reservoir into the pore, Fick's law requires a concentration gradient between reservoir and pore. This however is never the case for systems with an attractive interaction between fluid and pore wall. Thus, the driving force evaluated according to Fick's law as concentration gradient never points into the direction observed in experiment. In other words, Fick's law is not able to describe adsorption of a fluid from a gas reservoir into a pore.

On the other hand, Valiullin et al. explicitly state that they rely on Fick's law.² How can they do this if the driving force points into the wrong direction when evaluated as concentration gradient? The answer is easily found in a previous paper.³ The grand canonical gas reservoir is replaced by a porous reservoir made of the same material as the porous system.² The porous reservoir is filled with fluid so as to have the same chemical potential μ_{eq} as the gas reservoir. In case of adsorption, that is, if $\mu_{eq} > \mu_{(pore \text{ to be filled})}$, the concentration in the porous reservoir (as opposed to the gas reservoir) is higher than in the pore to be filled. It is important to note that Valiullin et al.¹ do not treat the experimental situation they claim to treat, namely adsorption

from gas phase into a porous system. Apparently they do this in order to be able to employ Fick's law. They do not give any proof that the replacement of one reservoir by a physically quite different reservoir is justified nor do they discuss this question.

In conclusion I state that Valiullin et al. have entirely overlooked the necessity to employ the correct driving force for diffusional transport.

At the end of this part, we inspect the general situation, that is, we start from eq (*) without specializing to $\beta = 1$. Then the explicit expression for the relaxation time is

$$\tau = \left(\frac{\beta}{t^{1-\beta}} \right)^{1/\beta} \frac{\beta}{t} \left(\frac{f(\infty) - f(t)}{\frac{df(t)}{dt}} \right)^{1/\beta}$$

The basic need to find the correct driving force in order to determine the rate of transportation $(df(t))/(dt)$ is the same as before.

Now we have a brief look onto the notion of Valiullin et al. that all systems which can be described by $\beta < 1.0$ (quenched disorder) are so totally different from the world of simple pores that results obtained for the latter have no impact unto the understanding of the first ones. First, the parameter β will hardly ever have the exact value 1.0. Wallacher et al.⁴ obviously have had the intention to prepare simple pores with constant diameter (A1 and A2) or with only two segments with diameters D_1 and D_s . The shape of the experimental isotherms led them to the conclusion that the practical realization of their pores was not as regular in shape as expected. This refers to the shape of the isotherms for A1 and A2 (hysteresis where no hysteresis was expected, or the H2 type hysteresis for all pores). Thus, when interpreting their data they have introduced the concept of quenched disorder caused by small variations δD in diameter. They consider their pores as large number of segments with different values of diameter D . From the desorption branch of their isotherms B and C, they are led, however, to the conclusion that δD must be small compared to the difference $D_1 - D_s$. The structure of the pores in silicon appears to be not as different from simple pores as claimed by Valiullin et al. The notion that small variations in pore diameter leads to H2 isotherms rather than H1 isotherms could be easily verified in simulations that I have carried out some time ago.

As conclusion I state on one side that the shape of isotherms is suited to characterize pore properties. On the other side, the attempt by Valiullin et al. to postulate two different worlds of simple pores versus mesoporous systems characterized by quenched disorder cannot be held up with respect to dynamic properties, cf. the discussion above.

References and Notes

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