CONFINED SYSTEMS WITHIN THERMODYNAMIC FRAMEWORK:TIME DEPENDENT VS. TIME INDEPENDENT TREATMENT

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Abstract

Porous material in contact with vapor tends to adsorb fluid in the pores. The amount of adsorbed fluid depends on the vapor pressure, but depends in some parameter ranges as well on the history of the system. When raising the vapor pressure the adsorption may be smaller than while lowering the pressure. Thus, the measured adsorption isotherm consists of two branches that appear stable on the time scale of experiments. The phenomenon is known as adsorption hysteresis and has been extensively discussed in the literature as it is in distinct contrast to the expectations of thermodynamics:the system has more than one answer to one set of boundary conditions (here: grand canonical boundary conditions). The common explanation offered in the literature introduces the concept of metastable states, conceiving either or both branches of the isothermas being metastable. Even though the concept of metastability cannot be separated from the concept of a lifetime against decay into the corresponding ground state, this aspect is usually not discussed in the literature. Within the adsorption community it is agreed upon that the concept of metastable states brings the experimental findings in harmony with the theory of thermodynamics while the lifetime of the conceived metastable states is disregarded. In the present paper we challenge this notion. We argue that the characteristic lifetime τ_{sys} of a system against decay into its ground state must be compared with the duration $\tau_{\exp}$ of the experimental technique employed to investigate the behavior of the system. Based on experimental evidence and based on previous theoretical results we find that the relation $\tau_{sys} >> \tau_{\exp}$ holds for typical adsorption systems. As thermodynamics is founded on the assumption $\tau_{sys} << \tau_{\exp}$ it cannot be the appropriate theory for describing adsorption systems.Several schemes found in the literature seem to provide such a time dependent approach. Our analysis, however, shows that neither of these attempts describes the time dependence in a realistic way. Thus, we have to conclude that no valid theory for the propagation of adsorption systems in time has emerged yet. We propose to develop a new generally valid time dependent theory for confined systems whose time independent limit for $\tau_{\exp}/\tau_{sys} \to 0$ would be suited to handle adsorption systems.

Keywords:

adsorption hysteresis · lifetime of metastable states · time dependent theory

1. INTRODUCTION.

THE PROBLEM WHEN TREATING ADSORPTION HYSTERESIS BY THERMODYNAMICS

The adsorption of fluids in porous material is of importance in various natural phenomena as well as in technical applications. Here we refer in particular to the situation where a vapor filled reservoir is in contact with porous material. In case of attractive interaction between fluid and material of the pore wall a substantial amount of fluid may be adsorbed by the inner surface of the porous solid. The amount of fluid that is stored inside the pores may in some ranges of pressure not only depend on the actual vapor pressure, but in addition on the history of the system. While the pressure goes up the amount adsorbed may be smaller than during decrease of the pressure.

As example we show in fig.1 the result of a computer simulation for adsorption of a fluid in a pore with two open ends in contact with the gas reservoir [1]. The parameters for the simulation are chosen to model argon at liquid nitrogen temperature adsorbed in the synthetic material SBA-15. The fact that the adsorption isotherm consists of two branches is named adsorption hysteresis and is known since more than 100 years.
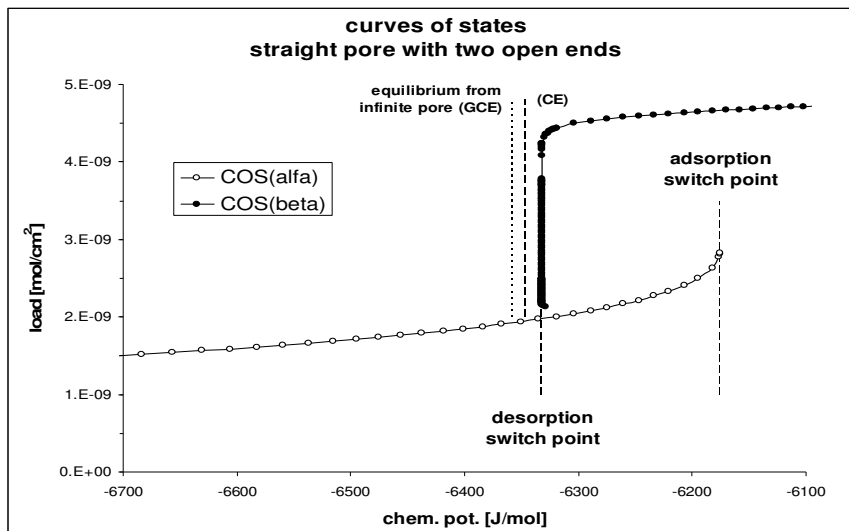
Fig.1 (adopted from ref.**Error! Bookmark not defined.**). The isotherm displays two separate branches for a straight pore with two open ends.

All experimental findings confirm that both branches of the isotherm are stable on the time scale of standard experiments. The notion that the states of the system may depend on the history is in distinct disagreementwith thermodynamics. Thermodynamics is based on the concept of state variables the most eminent property of which it is to depend exclusively on the actual boundary conditions and not on the experimental path leading to the actual situation.

All authors who have explicitly discussed the related theory have come to the conclusion that the phenomenon of adsorption hysteresis requires the postulate of metastable states.Metastability as explanation for the adsorption hysteresis has been discussed or mentioned over and over again in the literature. A few quotations are collected here: "Metastable states ...... appear to be the most important aspect." and "..in the experimental system the metastable states just do not have time enough to relax..." from ref.[2]or "...a failure of the system to equilibrate" and "This explains why hysteresis, although representing a departure from equilibrium, is so reproducible in experiment." from ref.[3]. In some papers the topic has been discussed at length [4]. From this work we quote only a short statement: "However, even in experiments in which accessible observation times are much longer than in simulations, a hysteresis is usually observed, whose properties are quite reproducible."

Studying literature one has to summarize that

- all authors consider the theory of thermodynamics to be the appropriate theory for handling adsorption systems

- all authors feel obliged to point out the existence of metastable states in order to bring the experimental finding of adsorption hysteresis into agreement with thermodynamics

- no author has attempted to come up with an estimate for the lifetime of the metastable states

The concept of metastable states is generally taken to be well suited in bringing experimental observation and thermodynamics into harmony. On the other hand, the concept of metastability cannot be separated from the notion that a ground state must exist into which a metastable state will decay with a characteristic lifetime.

Thus, postulating metastable states calls for a theoretical description that is suited to handle the time dependence of the system. Let us assume that the characteristic relaxation time of the system has the value τ_{sys}. Then it would be of interest to compare with the time scale τ_{exp} of the experiment that is used for studying the system.
Three cases could be encountered:

      1. Both times are the same order of magnitude, i.e. $\tau_{exp} \approx \tau_{sys}$. Accordingly the outcome of the experiment cannot be described by a time independent theory, but would require an explicitly time dependent treatment which cannot be thermodynamics, as it is a time independent theory

      2. The experiment takes much more time, i.e. if $\tau_{exp} >> \tau_{sys}$. In this case a time independent theory would be appropriate. Thermodynamics would be suited to describe the experiment.

      3. The experiment is very short compared to the characteristic time of the system, i.e. $\tau_{exp} << \tau_{sys}$. Then the system does not show changes during the measurement and again a (different) time independent theory is applicable. It is obvious, that this cannot be thermodynamics, as it is based on the assumption $\tau_{exp} >> \tau_{sys}$. In a previous paper [1] we have formulated the concept of Curves of States (COS) for this situation. It includes rules for the behavior of the system that reflect all known experimental findings.

The concept of COS is obviously to be understood as the limiting case of a time dependent theory in the limit $\tau_{exp}/\tau_{sys} \to 0$. The underlying time dependent theory does not yet exist in closed form. We feel, that the best approach to this end (i.e. to handling time in systems that are basically treated by thermodynamics) can be found in the many works that are occupied with homogeneous nucleation, e.g. [5,6,7]. On the other hand, the field of homogeneous nucleation considers fluctuations in an otherwise homogeneous environment, while adsorption systems have a strongly inhomogeneous distribution of matter even in the absence of fluctuations. Thus, the time dependent theory emerging from the above discussion is still to be developed. In this paper we will argue in favor of a proposition to develop a time dependent treatment for confined systems, in particular for those confined systems that can exist in more than one state for a given set of boundary conditions, i.e. for confined systems that display a hysteresis as shown in fig.1.
To our knowledge no generally valid theory has emerged yet for this purpose. We hold up this statement even though we are aware of several publications whose authors have dealt with confined systems and modeled in simulation calculations the transition between different branches of the isotherm [9,10,11,12]. We will argue that neither of these calculations is based on a realistic physical process, but that in fact purely mathematical approximations are employed.
The paper is organized as follows. In the next section we discuss some aspects of quantum mechanics, as this theory exists –by virtue of the Schrödinger equation– in a time dependent as well in a time independent version. Thus, quantum mechanics may serve as a paradigm for the goal of the present paper. The third section introduces to existing literature and contains a critical discussion thereof. The strategy that we assume to be fruitful in devising a generally valid theory that allows treating the time dependence of confined systems is presented in the fourth section. A last section contains an outlook and a short discussion of how the present topic is related to the topic of homogeneous nucleation.

2. QUANTUM MECHANICS AS A PARADIGM FOR TIME DEPENDENT VS. TIME INDEPENDENT THEORY

For quantum mechanical systems we are familiar with a time dependent as well as a time independent treatment, based on the corresponding Schrödinger equations. A frequently discussed example is a particle in a double well potential. The wavefunction that is determined via the time independent Schrödinger equation as eigenvalue problem is displayed in fig.2. The system can be treated as well via the time dependent Schrödinger equation. This solution would predict a periodic variation of the mean spatial coordinate with a frequency ω and a characteristic time $\tau_{sys} = \dfrac{2\pi}{\omega}$. The time average of this solution would reproduce the wave function in fig.2. If the experimental time scale $\tau_{\exp}$ is much longer than τ_{sys}, the time independent theory is suited for the treating the system. Classical quantum chemistry is formulated according to this scheme. τ_{sys} corresponds to the characteristic time of electronic motion while the characteristic time of nuclear motion provides the value for $\tau_{\exp}$. The relation $\tau_{\exp} \gg \tau_{sys}$ provides the justification for the Born-Oppenheimer approximation.
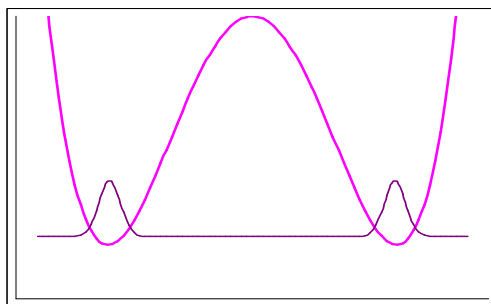

Fig. 2 Double well potential

On the other hand, there are experiments for which the relation $\tau_{\exp} \ll \tau_{sys}$ is assumed to hold. A well known example is x-ray photoelectron spectroscopy (XPS). The primary ionization process leads to the formation of an excited ion state A^{+*}

$$h\nu + A \rightarrow A^{+*} + e^- \tag{1}$$

which will further decay via fluorescence

$$A^{+*} \rightarrow A^+ + h\nu' \tag{2a}$$

or via the Auger process

$$A^{+*} \rightarrow A^{++} + e^- \tag{2b}$$

When evaluating spectra from XPS the decay paths (2a,b) are usually disregarded. In this case the time τ_{sys} is the lifetime of the excited ion A^{+*} while $\tau_{\exp}$ is to be understood as the time interval during which the interaction (energy exchange) between emitted electron and ion becomes negligible. The energy E_{el} of the emitted electron is interpreted as difference $E_{el} = h\nu - E_{bind}$ where E_{bind} characterizes the atom A and its chemical environment. The lifetime τ_{sys} can be read off the experimental spectrum via the natural line width. The center of gravity of the line is taken as E_{bind}. If quantum chemistry is employed to aid the interpretation, the excited ion state A^{+*} is treated as stable: the calculation does not include the coupling to the electromagnetic field thus prohibiting the decay path (2a), and the basis set contains only bound states thus excluding the decay path (2b). The outcome of the calculation is a sharp value for E_{bind} which is successfully equated to the center of gravity of the experimental peak. We note that the calculation employs meaningful approximations that allow making use of standard quantum chemical techniques. In the picture of the double well potential the corresponding approximations would consist in replacing the full potential by a single well potential, cf. fig.3.
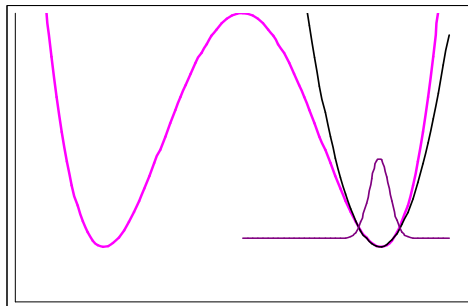
Fig.3

3.TREATMENT OF TIME EVOLUTION AS FOUND IN THE LITERATURE

3.1 Introductory remarks

For adsorption systems as shown in fig.1 the goal is to find the characteristic time τ_{sys} for the system to switch under constant grand canonical boundary conditions (i.e. under constant chemical potential μ_{ref} in the reservoir) between the two branches of the isotherm. The characteristic time may well be different in both directions (and usually is different). The equilibrium state of the system is taken on only on a time scale that is much longer than the longest value of τ_{sys}. The two branches of the isotherm are conceived to be separated by a high energy barrier and overcoming this barrier is a rare event. Thus, the lifetime against occurrence of the process is fairly long. As mentioned already above, there is no experimental evidence in typical adsorption systems that a switch between the two branches occurs at all, as long as the chemical potential μ_{ref} in the reservoir is kept constant. Accordingly, there is little hope thata characteristic lifetime τ_{sys} can easily be assessed experimentally for standard adsorption systems.

Indeed, the –to our knowledge–only theoretical attempt to calculate these lifetimesexplicitly [8]has lead to lifetimes many orders of magnitude larger than the age of the universe. This calculation is based on the model assumption that a fluctuation in the gas reservoir near the pore mouth is needed in order to drive the system under otherwise constant boundary conditions into the other branch of the isotherm. Thus, in this calculation the lifetime of the system depends on the average time one has to wait until a sufficiently large fluctuation occurs in the gas reservoir near the pore entrance. In view of the fact that the amount of matter inside the pore has to vary by a factor of about two, one can hardly expect that a fluctuation inside the pore without inflow from the reservoir can induce switching between different branches of the isotherm. The assumption made that a fluctuation outside the pore must drive the system appears convincing. Still, one could challenge this calculation by asking whether there may be fluctuations inside or outside the pore or a combination thereof that could lead to shorter lifetimes.

However, even if one assumes that employing different shapes of fluctuations could bring down the lifetimesby a few orders of magnitude, the absolute size of the lifetime would still exceed the age of the universe, thus underliningthat the thermodynamic assumption of $\tau_{exp} \gg \tau_{sys}$ is not fulfilled. It appears that a theoretical approachis needed to evaluate the respective lifetimes τ_{sys} reliably.

3.2. Attempts found in literature based on the Langevin equation

Several authors have studied switching between both branches of the adsorption isotherm by schemes based on the Langevin equation, e.g. [9,10,11,12]. Since we will argue that these attempts are not suited to calculate lifetimes τ_{sys}, we will shortly review basic ideas related to this equation.

The Langevin equation found in a common textbook [13] is a differential equation for the velocity $\vec{v}(t)$ of a particle driven by fluctuating internal forces $\vec{F}_{int}(t)$ and eventually by external forces $\vec{F}_{ext}$. It reads

$$m\frac{d\vec{v}(t)}{dt} = -\alpha \cdot \vec{v}(t) + \vec{F}_{int}(t) + \vec{F}_{ext} \tag{3}$$

where α is the friction coefficient and m the mass of the particle.
Often the Langevin equation is applied in order to handle the propagation of other quantities under influence of fluctuations. A typical form is

$$\frac{d\rho}{dt} = -\Gamma \cdot \frac{\delta F^{ex}(\rho(\vec{r}))}{\delta\rho} + \eta(\vec{r},t) \tag{4}$$

Here $\rho(\vec{r})$ stands for a scalar quantity depending on the location in the system and $\eta(\vec{r},t)$ denotes Gaussian noise, while Γ is a friction coefficient (named kinetic coefficient, dissipative coefficient or phenomenological friction coefficient). F^{ex} refers to the energy of the system, to be understood as functional of the scalar $\rho(\vec{r})$.

Following many authors, we will here specialize to $\rho(\vec{r})$ being the molar density in the system and F^{ex} being a thermodynamic potential (free energy or grand potential) of the system in excess of a standard situation.

We will now discuss the range of validity of both equations. Eq.(3) is well defined as it is based on Newton's law. The only approximation consists in assuming the friction to be proportional to the velocity [13] with a constant friction coefficient α. This is a mild and widely accepted approximation. Formally, eq.(4) looks very similar. If under grand canonical boundary conditions F^{ex} represents the grand potential, then it is obvious that the first part of eq.(4), namely

$$\frac{d\rho}{dt} = -\Gamma \cdot \frac{\delta F^{ex}(\rho(\vec{r}))}{\delta\rho} \tag{5}$$

is well suited to let a system relax towards its equilibrium by driving it towards the minimum of the grand potential. Under the influence of the noise $\eta(\vec{r},t)$ the system will not be in equilibrium and, thus, eq.(4) describes an ongoing competition between perturbation $\eta(\vec{r},t)$ and relaxation. If $\eta(\vec{r},t)$ describes continuous Gaussian noise, one may expect that eq.(4) is able to drive a system from one branch of the isotherm eventually over the barrier into another branch. This has indeed been successfully demonstrated by the authors of the papers quoted above, for various model descriptions of their systems and different boundary conditions [9,10,11,12].

Still, we claim that the Langevin equation in the form of eq.(4) is not the final answer to the attempt to calculate the lifetime τ_{sys} in an adsorption system. Our criticism is based on the notion that the relaxation part of the Langevin equation, i.e. the eq.(5) does not describe physical transport, but rather represents a mathematical algorithm that actually drives a system into equilibrium, but does not do so along a physical path. Therefore, even if eq.(5) explores possible pathways into equilibrium the related equation eq.(4) hardly yields any information on the real time behavior.

For comparison, we will now address an equation that is explicitly meant to describe physical transport. It is the Onsager ansatzfor diffusion which reads for isothermal systems

$$\vec{J} = -\frac{L}{T} \cdot grad\mu \tag{6}$$

In order to establish a more obvious relation to the form of theLangevin equation (4) we employ the continuity equation

$$\frac{d\rho}{dt} = -div\vec{J} \tag{7}$$

This turns equation (6) into

$$\frac{d\rho}{dt} = \frac{L}{T}\Delta\mu \tag{8}$$

Undoubtedly, the equations (6) or (8) are able to drive a system into equilibrium which is represented by constancy of the chemical potential which in turn is equivalent to minimizing the thermodynamic potential corresponding to the boundary conditions chosen.

In principal one could add the noise term from eq.(4) to eq.(8) to obtain

$$\frac{d\rho}{dt} = \frac{L}{T}\Delta\mu + \eta(\vec{r},t) \tag{9}$$

Eq.(9) can drive a system over a barrier as can be done with the aid of eq.(4). We are not aware of any author who has attempted to do so. In the following we will compare the properties of the two equations (5) and (8) by means of numerical calculations on a pressure jump [8]. This process refers to an experiment which starts on COS(α) which is the vapor filled branch of the isotherm, cf. fig.1. At the beginning of the experiment the pressure in the reservoir is raised to a value so high that the system is forced to switch into the liquid filled branch COS(α). The relaxation of the system into the new equilibrium has been simulated via eq.(6) in ref.[8] and will now be computed via eq.(5) for comparison. We will describe explicitly the procedure we have carried out. The thermodynamic potential used in eq.(5) is the grand potential

$$\Omega = -\int \rho(\vec{r}) \cdot (\mu(\vec{r}) - A_m(\vec{r}))d^3r$$

After the pressure and thereby the density in the reservoir is set to the new final value, the new reference value of the chemical potential is the corresponding value $\mu_{final} = \mu(\rho_{final})$. Accordingly, we define the grand potential with reference to the new value of the boundary condition μ_{final} as

$$\Omega^{ex} = -\int \rho(\vec{r}) \cdot (\mu_{final} - A_m(\vec{r}))d^3r$$
$$= -\mu_{final} \cdot \int \rho(\vec{r})d^3r + \int \rho(\vec{r}) \cdot A_m(\vec{r})d^3r$$

Thus, eq.(5) transforms into

$$\frac{d\rho}{dt} = -\Gamma \cdot \frac{\delta\Omega^{ex}(\rho(\vec{r}))}{\delta\rho} \tag{10}$$

For a localized variation $\delta\rho$, i.e. for a variation that vanishes outside a small region near $\vec{r}$ we can make use of the partial derivative of Ω^{ex} to obtain

$$\frac{d\rho}{dt}(\vec{r}) = -\Gamma \cdot \frac{\partial\Omega^{ex}(\rho)}{\partial\rho}(\vec{r}) \tag{11}$$

This expression develops into

$$\frac{d\rho}{dt}(\vec{r}) = -\Gamma \cdot \left(-\mu_{final} + A_m(\vec{r}) + \rho(\vec{r})\left(\frac{\partial A_m}{\partial \rho}(\vec{r}) \right) \right)$$
$$= -\Gamma \cdot \left(\mu(\vec{r}) - \mu_{final} \right)$$

The increment of the density at the location $\vec{r}$ during a time step dt is then

$$d\rho(\vec{r}) = -\Gamma \cdot dt \cdot \left(\mu(\vec{r}) - \mu_{final} \right) \qquad \textbf{(12)}$$

Eq.(10) will drive the system towards a minimum of the grand potential which at the same time causes the chemical potential to take on everywhere the reference value μ_{final}. The speed of this approach to equilibrium is controlled by the product $\Gamma \cdot dt$. We have adjusted $\Gamma \cdot dt$ in such a way that the outcome of the calculation does not depend any more on the size of $\Gamma \cdot dt$. Within this side condition its value has been chosen as large as possible in order to save computer time. We find that the computational effort needed to letthe system relax is by about 3 orders of magnitude smaller for eq.(5) than for eq.(8).
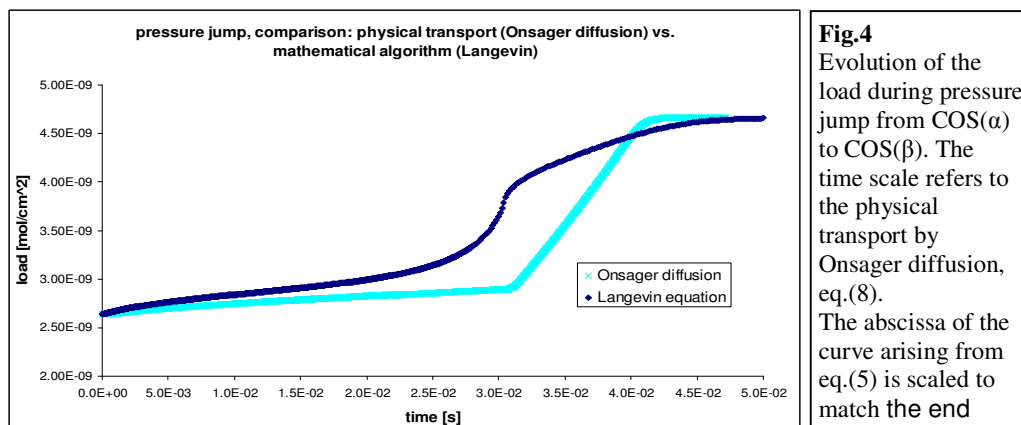
Fig.4
Evolution of the load during pressure jump from COS(α) to COS(β). The time scale refers to the physical transport by Onsager diffusion, eq.(8).
The abscissa of the curve arising from eq.(5) is scaled to match the end

Even though both equations drive the system into the same final state, namely the equilibrium state corresponding to μ_{final} on the branch COS(β), we find that the trajectory created by eq.(5) differs strongly from the trajectory generated by eq.(8). As displayed in fig.4, the development of the load with time in case of Onsager diffusion and under the Langevin equation are both monotonic, but clearly not identical. The discrepancies between both trajectories become more apparent if we inspect the evolution of the chemical potential. Start and end points of the trajectories refer to stable states with a well defined value of the chemical potential. Along the trajectories, however, we have transient situations that are characterized by gradients of the chemical potential and thereby by a distribution of the chemical potential. In order to indicate the spectrum of the values for any time step in the calculationwe have evaluated the minimum, the maximum and the averaged value of the chemical potential. For any step in the trajectories we know the values of the chemical potential together with the actual load. Consequently, we are in the position to plot load and chemical potential against each other. In this way, the trajectories which represent a sequence of transient situationscan be inserted into the plot of the isotherms which represent stable states, cf.fig.5.
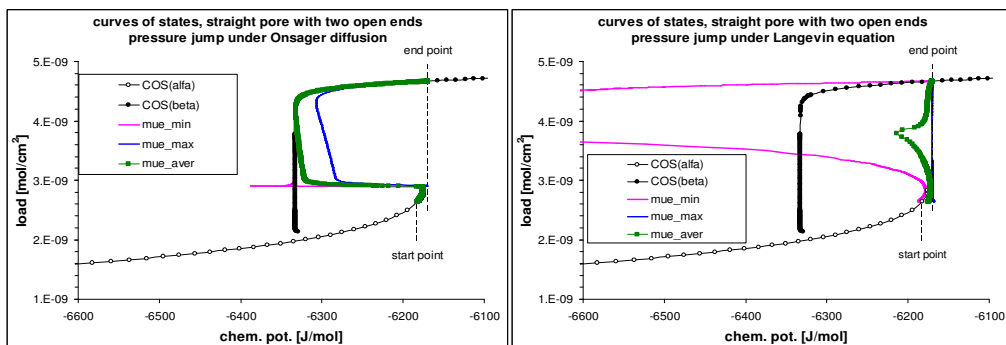
Fig.5. The trajectories of the pressure jumps are inserted into the plot of the isotherm. Left panel: trajectory resulting from the physical transport process of Onsager diffusion. Right panel: the trajectory computed with the eq.(5) or eq.(12)

The trajectory resulting from the physical transport of Onsager diffusion carries out a distinct jump from COS(α) into COS(β) as soon as the load exceeds the maximum load that can be accommodated in COS(α). In ref. [8], this load has been named PONR (=Point of no Return). It turned out to be quite insensitive to the choice of starting and final states. The system, when modeled by the physical transport process, displays a fairly narrow spectrum of values of the chemical potential, as can be read off the fact that the three curves lie comparatively close together. This is different for the trajectory resulting from eq.(5) or eq.(12). Minimum and maximum are widely separated. Inspecting the averaged values of both trajectories displays another remarkable difference: while the averaged value from the physical trajectory follows the isotherm with a sudden jump between the two branches at the PONR, the non-physical trajectory does not care at all about the positions of the isotherm. In contrast, the non-physical trajectory moves directly through the range lying between starting and final point that the physical trajectory so carefully avoids.
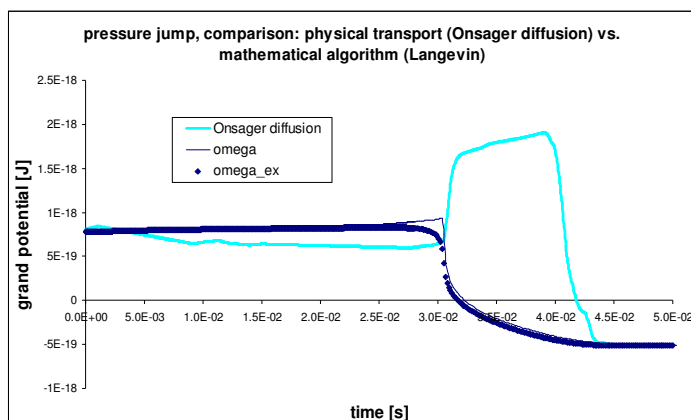
Fig.6 The grand potential behaves differently between the Onsager diffusion and the non-physical trajectory. In the latter case we have plotted the grand potential Ω and Ω^{ex} which is the grand potential defined with reference to the boundary condition μ_{final}. Both quantities differ only little compared to the common difference to the

Fig. 6 compares the variation of the grand potential during the trajectories. Start and final values are identical for both algorithms, of course. We observe, however, that Onsager diffusion leads to a high barrier of the grand potential before it drops to its final value. The non-physical transport on the other hand, displays only a weak barrier. The differences between Onsager diffusion and Lange in equation as displayed in fig.5 and fig.6 nicely reflect the different strategies underlying both approaches. Eq.(5) and eq.(10) and, thus, the working formula in eq.(12) are designed to minimize the grand potential. We are not surprised to observe that the barrier found in fig.6 for the related trajectory is very small compared to the Onsager trajectory. On the other hand, the eq.(6) and (8) pursue the goal to minimize the gradient of the chemical potential. This behavior is clearly retrieved when inspecting the fig.5.The spectrum of the chemical potential is much more narrow at any given load compared to the propagation based on eq.(10).

In consequence, it is not surprising that the simulation of a transition from one branch of the adsorption isotherm to the other is much easier achieved by eq.(4) than by eq.(9). Indeed, this strategy is commonly used in this field[9,10,11,12], while eq.(9) has –to our knowledge– never been the basis for the simulation of a fluctuation driven transition between branches of the adsorption isotherm.

As the outcome of both strategies is clearly different, one has to decide which strategy is correct. We wish to point out that eq.(8) and eq.(9) are based on a real physical transport process, while eq.(4) is only a formal adaption of the Langevin equation. The authors who make use of eq.(4) point out that they relate the friction coefficient Γ to the Gaussian noise $\eta(\vec{r}, t)$ by means of the fluctuation-dissipation-theorem[13]. We claim, however, that this is a purely formal approach as there is no underlying real transport process. If we compare the equations (4) and (9), we have to state that eq.(9) is based on the Onsager ansatz for diffusion in eq.(6) which can be proven to be realistic by comparison to experimental data. In simple cases, this ansatz reduces to the familiar formula for diffusion by Fick. If eq.(4) or eq.(5) would be claimed to be a likewise valid approach one would have to come up with a related transport process and a related transport equation which could then be converted into eq.(5) by virtue of the continuity equation. The transport quantity were to be expressed again by the current density of amount as in eq.(6), but which quantity could play the role of the driving force?

We have to conclude that the equation (5) does not describe a physical process. It presents a purely mathematical algorithm that has the power to relax a system into its equilibrium while the trajectory lacks physical significance. In view of these results we suggest that an equation of the form of eq.(4) should not be referred to as Langevin equation, as the original equation named after Langevin, i.e. eq.(3) is of physical relevance. Maybe one should call eq.(4) a Langevin-like equation in order to avoid to assign the non-physical nature of this equation to Langevin.

3.3. Attempts found in the literature based on Grand Canonical Monte Carlo simulations

In eq.(6) we observe the presence of the gradient of the density which relates neighboring sites in the system and causes transport by diffusion. In the Langevin equation in the form of eq.(4) this relation between neighboring sites is missing. Undoubtedly, the functional $F^{ex}(\rho(\vec{r}))$ depends on the density $\rho(\vec{r})$ in the entire system, but this fact does not lead to a realistic description of transport in the system. Thus, the probability for a situation to occur in the calculation via eq.(4) is governed by its energy, but not by the time needed for transport of matter.

This latter feature is closely related to simulations where GC Monte Carlo method is employed to model transitions from a metastable to another state. An instructive example has been presented by Neimark and Vishnyakov [14]: for a spherical pore they carry out simulation calculations on the transition from a vapor filled state into a liquid filled state. The spherical pore has a virtual interface to a gas reservoir, held at constant vapor density. The GC MC steps make particles move, but allow as well the appearance of additional particles. The acceptance or non-acceptance of all steps depends on the energy criterion. Thus, the appearance of an additional particle does not take into account the need to transport this additional particle from the reservoir into the pore and the time it would take to achieve this transport. While the assumption of a linear relation between time steps and real time is justified for canonical MC, it certainly is not for GC MC. Only the final result of a GC MC calculation is well defined, but if GC MC is employed to describe the time dependence, one has to realize that the time that corresponds to a single time step may vary by orders of magnitude with the actual situation. We clearly recognize the similarity between the strategies based on eq.(4) and the GC MC scheme.

4. SEARCH FOR A GENERALLY VALID TIME DEPENDENT TREATMENT FOR ADSORPTION SYSTEMS

The attempts reported above from literature describe the propagation of a system under the influence of fluctuations over the energy barrier into another state. We have argued that this approach does not reveal the behavior in real time. Thus, even though some of these attempts demonstrate the oscillation between two states within a finite number of computational steps, no

real time can be related to this oscillation and, accordingly, the authors have not tried to evaluate a characteristic time scale τ_{sys} for their systems.

For the time dependent theoretical description of adsorption systems no generally valid theory has emerged yet. We are interested in systems that can exist in more than one situation for a given set of boundary conditions, i.e. which display a hysteresis, cf. fig.1. While in quantum mechanics the mechanism that could drive the system between two or more situations is well known as tunneling and handled by the theory, for adsorption systems the theoretical techniques are less unambiguous.

From experiment it is known that both branches of the adsorption hysteresis appear stable during typical experiments. Accordingly, one cannot expect to find a spontaneous decay of either of the branches in a run of a standard computer simulation. If one wishes to come up with an estimate for the lifetime of both branches of the hysteresis loop, one has to have information along which path and by which mechanism the system will switch from one branch to the other. In ref. [8] we have studied the transition from one branch to the other by simulating pressure jumps. This strategy revealed the mechanism by which the system performs the switch.

If one wishes to study the transition under constant boundary conditions one would have to rely on fluctuations to drive the system over a barrier into an alternative situation. Useful fluctuations have to fulfill certain conditions: they must be strong enough to drag the system over the barrier and, among all fluctuations fulfilling this requirement, we are interested in finding the ones that occur most readily. The average waiting time for a fluctuation strong enough to enable the transition could be considered as lifetime against decay into the new situation. In the investigation mentioned above [8] we have varied the amplitude and the extension of the fluctuation. The mean time one has to wait for the smallest fluctuation strong enough to perform the switch has then be adopted as lifetime of the state under investigation.

Unfortunately, there is so far no general way to estimate which fluctuation is best suited for the task. Thus, one can try out in computer simulation different shapes of fluctuations in order to find the most effective fluctuation. Thus, the search for a generally valid time dependent theory of adsorption may to a large degree be the development of a systematic search for the most effective fluctuation to cause the transition from a given start point to a given end point.

5. CONCLUSION AND OUTLOOK

Thermodynamics is the only physical theory that does not contain time. The implicitly underlying assumption is that this theory describes the situation of a system at times much longer than the intrinsic time scale τ_{sys}. However, as soon as the notion of met stability comes into play, this assumption cannot be accepted any more as discussed in the sections above. Metastable states are known and discussed not only for confined systems, but as well for systems that are large enough to fulfill the thermodynamic limit.

In the latter case, it is well known that for certain parameter ranges the thermodynamic equilibrium state is a coexistence state. The formation of a coexistence stateproceeds via the process of nucleation. This process is known to require time, and its probabilityis expressed bythe rate of creation of nucleation centers, e.g. creation of droplets in a supersaturated vapor. The nucleation rateis successfully treated by homogeneous nucleation theory [5,6,7] and is

investigated experimentally [15] by exploring the onset of nucleation under various experimental conditions. The thermodynamic concept is the following: if one raises the vapor pressure of a condensable fluid beyond a threshold value (saturation pressure) condensation sets in leading to coexistence states. Accordingly, the process of nucleation should be a key feature of thermodynamics, because without nucleation a system could not behave according to thermodynamic expectation. In spite of this consideration one observes that usually nucleation theory is not conceived to be closely related to thermodynamics, even though the accepted rules of thermodynamics require nucleation to happen. In other words, a time dependent process is necessarily involved to make the time independent theory of thermodynamics a valid description of corresponding systems.

With respect to confined systems, we have found a similar situation: without a time dependent treatment the description of adsorption systems remains incomplete. Inspection of what is known on confined systems, in particular the adsorption systems discussed in the previous sections, leads to the notion of metastable states and to the necessity to occupy oneself with time dependence. The goal of the present paper is to propose developing a time dependent theory for treating confined systems in case of $\tau_{sys} \approx \tau_{\exp}$ and to establish the two time independent schemes for

$\tau_{sys} \gg \tau_{\exp}$ and $\tau_{sys} \ll \tau_{\exp}$.

Whether in the long run this time dependent theory for confined systems and the well developed nucleation theory for large homogeneous systems can be merged, is difficult to predict, but would certainly be desirable.

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