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Short communication

Stability of the kaolinite-guest molecule intercalation system: A molecular simulation study

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ABSTRACT

Molecular dynamics and Monte Carlo simulations are used to determine the stable states of the kaolinite-methanol intercalation system. Several evaluation scenarios are presented to describe the stability of the system using single $\mu_{\mathrm{Solvent}}N_{\mathrm{Clay}}pT$ ensemble simulations and a series of NpT ensemble simulations coupled with thermodynamic integration.

1. Introduction

Clay minerals with layered structure on the molecular level are capable of adsorbing organic and inorganic guest molecules in their interlayer space. The phenomenon itself is referred as intercalation and it is of interest due to its possible application in the design of many clay mineral based nanomaterials. These materials are promising candidates for catalysts, adsorbents, and composites [1]. When synthesizing nanomaterials from layered clays, the effect of the intercalated molecules on the layers is diverse. They can change the surface properties of the mineral layers due to chemical reactions, or simply make the interlayer space expand for other molecules to enter that do not intercalate directly by themselves. At some point, it also becomes essential that the guest molecules completely push the molecular layers apart producing delaminated layers that can form various nanostructures such as curled layers, tubes, or scrolls. Although kaolinite is one of the most common layered clay mineral found in nature and used routinely in the paper, ceramic, medicine, and cosmetic industry, its role as building block for the construction of nanomaterials, compared to other expandable layered materials [2] has been less prominent, yet successful [3,4]. The reason behind this is that the clay layers in kaolinite are held together by hydrogen bonds in its pure mineral form and only a few highly polar molecules, such as hydrazine, urea, potassium acetate, formamide, and dimethylsulfoxide, can be used as a direct expansion compound [5,6]. On the other hand, exactly the dipolar character of the interlayer spaces makes kaolinite so appealing for materials design purposes. The range of potential guest species can be considerably extended by applying intermediate substances. These molecules displace the initially intercalated highly polar ones. After that, they are replaced by long-chain organic molecules in subsequent steps. This finally causes the complete separation of the kaolinite layers. Methanol has proven to be such an important intermediate [3,4,7] and it is the target of the current investigation. In this work, we model the methanol-kaolinite intercalation mixture without the possible chemical reactions between the surface of the clay layers and methanol [3,4,7,8]. The results presented here serve as a clear staring point and reference for further investigation purposes.

2. Methods of choice

Molecular simulation has evolved to point where it can effectively contribute to the understanding and detailed description of a variety of engineering related processes including the swelling of clay minerals [9,10]. It has an advantage over many experimental

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methods that it offers immediate insight on the molecular level and it is not limited by extreme conditions. Thanks to the rapid development of high performance computing, it is already possible to simulate the initial phase of the delamination/exfoliation of nanolayers with a realistic kaolinite layer size in real time [11]. Nevertheless, massively parallel supercomputers are still not available for everyday use, not even in academic research. In terms of evaluating the stability of a given kaolinite-solvent system, the general intercalation phenomena of clay minerals can be targeted with various simulation scenarios that involve considerably less computational effort. Still, careful planning or preceding experience is often necessary to be fully aware of the pros and cons of the selected approaches.

Generally, the most simple and convenient choice is to perceive the kaolinite-solvent mixture as a result of a special phase equilibrium between the bulk phase of the solvent fluid (gas or liquid solvent) and that of the mixture. The obvious simulation setup for this scenario consists of two simulation boxes: one box represents the homogeneous bulk phase of the solvent molecules; the other contains both the solvent and an arbitrary segment of the crystallographic structure of kaolinite (which is essentially molecular layers of kaolinite stacked upon each other with solvent molecules between these layers). This configuration is repeated in all three spatial directions through periodic boundary conditions. To ensure thermodynamic equilibrium, the pressure p and the temperature T of the two systems are set to identical values. Whether the equality of the chemical potential μ of the solvent molecules with respect to the two phases is ensured in separate constant chemical potential ensemble simulations or using a Gibbs ensemble setup [12,13], it is irrelevant for the current purpose. In any case, to capture the swelling nature of the clay, it is sensible to model the phase containing it using a $\mu_{\mathrm{Solvent}}N_{\mathrm{Clay}}pT$ ensemble. In such simulation, the volume of the system V that corresponds to the external pressure p is restricted to change only along the axis normal to the layers. The chemical potential of the solvent molecules μ_{Solvent}, the pressure p, and the temperature T are held constant and match those of the bulk phase while the number of particles N for the clay mineral is also constant. In a single classical molecular simulation, an ensemble is guaranteed to sample the equilibrium state (or an equilibrium state if there are more than one) of the model system. In intercalation experiments, the kaolinite-solvent mixture is traditionally characterized by the basal spacing d (distance between two consecutive layers) and the solvent content between layers (often referred as loading). These properties can be conveniently obtained as simple ensemble averages using the $\mu_{\mathrm{Solvent}}N_{\mathrm{Clay}}pT$ ensemble. This method was successfully applied to predict the basal spacing and loading for variety of intercalation systems for small polar solvent molecules and the obtained results showed promising agreement with available experimental data [14]. Unfortunately, the efficiency of a constant chemical potential ensemble calculation is limited by the size of the solvent molecules, because the number of successful particle insertions/deletions, required for trustworthy statistical results, decreases drastically with the increasing molecular size of the solvent in spatially confined systems for a given runtime. Another drawback of the $\mu_{\mathrm{Solvent}}N_{\mathrm{Clay}}pT$ ensemble approach is that, although it finds equilibrium state(s), it cannot give further information around the minimum about the shape of the energy surface that is defined by other solvent loadings and corresponding basal spacings.

A simple method to obtain a general view with respect to stability of different compositions is to perform a series of NpT ($N_{\mathrm{Solvent}}N_{\mathrm{Clay}}pT$) ensemble simulations with increasing solvent content N_{Solvent} and plot N_{Solvent} in function of the basal spacing d that is obtained as an ensemble average (cf. Fig. 1 top). A basal spacing range represents a stable state if d does not change substantially with solvent content. Due to its simplicity, this approach is a straightforward choice of simulation works [15–18]. However, in order to be able to properly comment on the stability of states at constant N, p and T, the corresponding Gibbs free energy profile or equivalent information is required. The local minima of the system's Gibbs free energy G are indicated by the first and second derivative tests. Namely, $\mu_{\mathrm{Solvent}} = \partial G/\partial N_{\mathrm{Solvent}} = 0$ (for which μ_{Solvent} must be smaller than zero left and larger than zero right from the local minimum) and $\mu'_{\mathrm{Solvent}} = \partial \mu_{\mathrm{Solvent}}/\partial N_{\mathrm{Solvent}} > 0$ around the minimum while N_{Clay}, p, and T are constant [19]. In molecular simulations, the residual chemical potential can be calculated, in principle, directly by Widom's particle insertion method [20]. However, the method requires sufficient amount of particle insertions without overlaps, which practically cannot be achieved in spatially confined systems such as the one containing

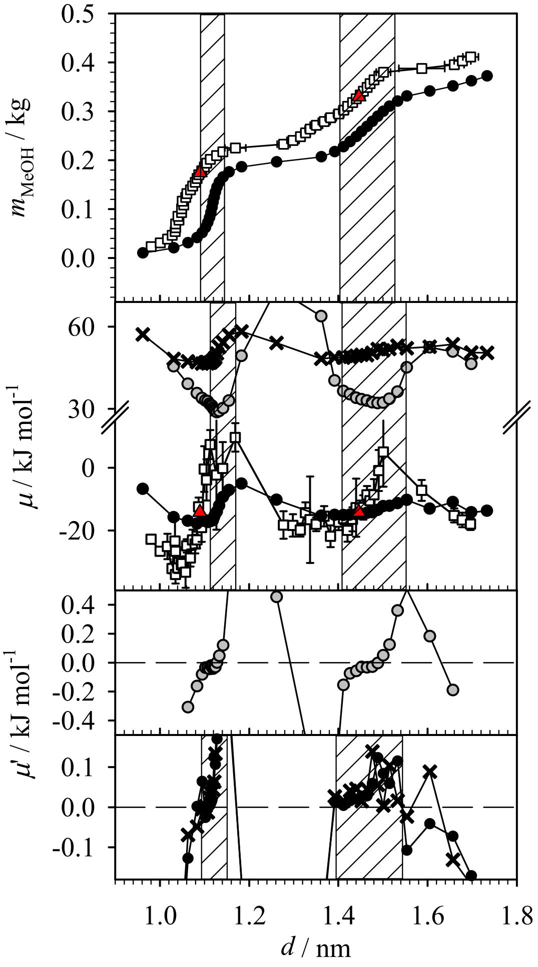

Fig. 1. Molecular simulation results for the chemical potential μ of methanol (MeOH) calculated by thermodynamic integration and for basal spacing d in the kaolinite-methanol system. m_{MeOH} denotes the methanol content in 1 kg of kaolinite. White squares: series of NpT ensemble simulations with setup (I). Red triangles: $\mu_{\mathrm{Solvent}}N_{\mathrm{Clay}}pT$ simulations with setup (I). Circles and crosses: series of NpT ensemble simulations with setup (II). Circles represent results, with setup (II), that do not consider contributions from internal degrees of freedom as opposed to crosses. Grey circles represent the approximation $\mu_{\mathrm{conf}} \approx \partial H_{\mathrm{conf}}/\partial N_{\mathrm{MeOH}}$. Both $\partial H_{\mathrm{conf}}/\partial N_{\mathrm{MeOH}}$ and $\mu' = \partial\mu/\partial N_{\mathrm{MeOH}}$ were obtained by numerical differentiation. Note that the exclusively temperature dependent ideal contribution $\mu_{\mathrm{id}}(T)$ (which includes internal degrees of freedom) cancels out in this derivation step. The detailed description of setups (I) and (II) can be found in the text. In the ideal contribution $RT\ln(\rho/\rho_{\mathrm{reference}})$, $\rho = N_{\mathrm{MeOH}}/V$ nm^{-3} and $\rho_{\mathrm{reference}}$ was 1 nm^{-3}. For the black circles, dashed areas indicate the regions in which stable states are located based on the individual subplots; their joint segments help to narrow down these regions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).