Systematic microcanonical analyses of polymer adsorption transitions

Monika Möddel, Wolfhard Janke and Michael Bachmann

Received 10th February 2010, Accepted 14th May 2010
DOI: 10.1039/c002862b

In detailed microcanonical analyses of densities of states obtained by extensive multicanonical Monte Carlo computer simulations, we investigate the caloric properties of conformational transitions that adsorbing polymers experience near attractive substrates. For short chains and strong surface attraction, the microcanonical entropy turns out to be a convex function of energy in the transition regime, indicating that surface-entropic effects are relevant. Albeit known to be continuous transitions in the thermodynamic limit of infinitely long chains, the adsorption transition of nongrafted finite-length polymers thus exhibits a clear signature of a first-order-like transition, with coexisting phases of adsorbed and desorbed conformations. Another remarkable consequence of the convexity of the microcanonical entropy is that the transition is accompanied by a decrease of the microcanonical temperature with increasing energy. Since this is a characteristic physical effect it might not be ignored in analyses of cooperative macrostate transitions in finite systems.

1 Introduction

The advances in processing and manipulating molecules at solid substrates on the nanometre scale opens up new vistas for technological applications of hybrid organic-inorganic interfaces. This includes, e.g., the fabrication of nanostructured transistors being sensitive to specific biomolecules and the application of organic electronic devices based on polymers such as organic light-emitting diodes and molecular storage cells. Therefore, the investigation of molecular self-assembly near substrates has recently been the subject of numerous experimental and computational studies, e.g., for peptide adhesion to metals and semiconductors. The understanding of the cooperative effects of structure formation at substrates requires systematic studies of mesoscopic aspects of adsorption transitions. This includes scaling properties near the adsorption/desorption transition in the thermodynamic limit of large polymer systems at planar surfaces, also under pulling force. Adhesion studies of polymers were also performed at curved surfaces such as nanotubes and nanoparticles. Particular attention has been dedicated to the complete phase structure of adsorbed macromolecules which has been investigated by means of simple lattice models for polymers and peptides as well as by employing an off-lattice polymer model.

Hybrid systems on the nanoscopic scale must basically be considered as being “small”. Thus, the study of finite-size effects in the formation of polymer assemblies in a thermal environment is relevant. Here, we are going to discuss thermodynamic properties of the adsorption transition of a flexible, interacting polymer at an attractive substrate. The polymer is not anchored at the surface and can therefore freely move as long as it does not get into contact with the substrate. Statistical analysis is performed in the microcanonical ensemble in order to retain characteristic, non-negligible surface effects. This approach has already proven quite useful for a deeper understanding of first-order-like structural transitions such as molecular aggregation processes and protein folding.

A particularly striking result was the recent identification of intrinsic hierarchies of subphase transitions that accompany the overall cooperative process of assembly. The relevance of microcanonical thermodynamics in small-system transitions has also been stated in simulational and experimental atomic clustering studies, fragmenting nuclei, and for scaling analyses in magnetic systems employing discrete or continuous spin models. A more exotic example is the seminal application of this approach to astrophysical systems, which manifests its broad universality.

The central quantity in the microcanonical formalism is the number (or density) of states $g(E)$ with system energy $E$, or the microcanonical entropy defined as

$$S(E) = k_B \ln g(E),$$

where $k_B$ is the Boltzmann constant. In contrast to canonical $(NVT)$ statistics, where the temperature $T$ is an externally fixed control parameter, in the microcanonical $(NVE)$ ensemble it is derived from the entropy,

$$T(E) = \frac{\partial S(E)}{\partial E}.$$

In both ensembles, the particle number $N$ and the volume $V$ are kept fixed. Particularly interesting microcanonical effects occur in the transition regime, if the entropy is a convex function of energy in this region. The physical consequence is that with increasing system energy the temperature decreases. This can only be explained by the fact that conformational transitions of small systems are governed by...
their surfaces, whereas volume effects become only relevant for large systems [even a perfectly icosahedral atomic cluster with 309 atoms still contains more atoms in the outer shell (162) than in the interior (147)].

Thus, as long as the surface-to-volume ratio is large enough to suppress a concave increase of the microcanonical entropy and the energetic separation of the two distinct phases [one of which is entropy-dominated (e.g., liquid) and the other energy-dominated (e.g., solid)] is sufficiently large to establish a kinetic barrier, microcanonical effects matter. This regards all first-order phase transitions and two-state systems (e.g., proteins with two-state folding characteristics). It also matters for transitions, where phase co-existence is completely absent in the thermodynamic limit, but not for the finite systems. The latter case is what we would like to consider in more detail in the following: the adsorption transition of flexible polymers to an attractive substrate, known to be a second-order phase transition in the thermodynamic limit. However, as we will show here, the adsorption of nongrafted polymers with finite lengths exhibits signals of a first-order transition which we find to vanish in the thermodynamic limit.

2 Model and methods

For our analysis, we consider a single flexible and nongrafted linear homopolymer with $N$ monomers that interacts with an attractive planar substrate. In ref. 30, we have already employed this hybrid model for the strictly canonical identification of conformational adsorption phases. Here, we concentrate ourselves on the adsorption/desorption transition between desorbed (DE) and three-dimensional adsorbed (AE2) expanded conformations (see Fig. 1), where “three-dimensional” refers to the topology of the dominant adsorbed conformations in AE2, extending into directions parallel and perpendicular to the substrate (in contrast to the preferably planar structures in AE1).

The polymer is represented by a bead-stick model with standard Lennard-Jones (LJ) interaction between nonbonded monomers, mimicking short-range volume exclusion and long-range van der Waals (vdW) attraction. Bond lengths between adjacent monomers are normalized to unity. Since the original model (called the “AB model”)$^{145,146}$ was designed for mesoscopic heteropolymers, an additional weak bending energy was introduced which is kept here. The only degrees of freedom in our polymer model are thus the angles between successive bonds. Center-of-mass translation is restricted to a cavity bounded by the attractive substrate located at $z = 0$ and a sufficiently distant steric wall at $z = L_z$ to prevent the polymer from escaping. Later in this paper we will discuss the dependence of the microcanonical results on $L_z$ in detail. If not mentioned otherwise, the monomer density is kept constant, i.e., $L_z$ scales linearly with the length of the chain $N$ (we chose $L_z = 3N$, i.e., a constant concentration of monomers). Translation in the $xy$-plane parallel to the walls is irrelevant here.

The interaction of a monomer with the continuous flat surface of a substrate filling the half-space $z \leq 0$ is obtained by integrating a 12-6-LJ potential over this half-space, which results in a 9-3-LJ-like potential.$^{30,47}$ In our simulations, all energies in units of a global energy scale $e$ are used:

$$E = 4 \sum_{i=1}^{N-2} \sum_{j=i+2}^{N} (r_{ij}^{12} - r_{ij}^{-6}) + \frac{1}{4} \sum_{i=1}^{N-2} \left[1 - \cos(\theta_i)\right]$$

$$+ \frac{4}{15} \sum_{i=1}^{N} \left( \frac{2}{3} z_i^3 - z_i^3 \right),$$

where $0 \leq \theta_i \leq \pi$ denotes the bending angle between monomers $i$, $i+1$, and $i+2$. The distance between the monomers $i$ and $j$ is $r_{ij} = |\vec{r}_i - \vec{r}_j|$ and $z_i$ is the distance of the $i$th monomer from the substrate. The free parameter $e_\alpha$ represents the surface attraction strength and weights the energy scales of monomer–surface ($E_{\text{surf}}$) and intrinsic monomer–monomer ($E_{\text{bulk}}$) interaction.

In order to improve the sampling of entropically suppressed energetic states, simulations of this model were performed with the multicanonical Monte Carlo method,$^{48}$ which is based on a generalized ensemble where the energy histogram is constant and hence directly yields an estimate for the density of states $g(E)$. This can be achieved by Monte Carlo sampling of polymer conformations $X$ with the transition probability

$$c(X \to X') = \min[W_{\text{mc}}(E(X'))/W_{\text{mc}}(E(X)), 1],$$

where $W_{\text{mc}}(E(X)) = g^{-1}(E(X))$ is the multicanonical weight function. Since $g(E)$ is obviously unknown in the beginning,
$W_{\text{micro}}(E(X))$ has to be determined recursively. Starting, e.g., with $W^{(0)}_{\text{micro}}(E) = \text{const}$, the energy distribution is almost "flat", if the estimate for the density of states after the $n$th run, $g^{(n)}(E)$, satisfies
\begin{equation}
   g^{(n)}(E)W^{(n-1)}_{\text{micro}}(E) \approx \text{const}.
\end{equation}
An efficient, error-weighted estimation method for $W_{\text{micro}}(E)$ is discussed in ref. 49. The recursion scheme can be stopped if the weight function estimate has stabilized. Then, the density of states $g(E)$ can finally be measured in a long multicanonical production run based on these weights.

Exemplified for a polymer with 20 monomers and a surface attraction strength $e_a = 5$, we have plotted in Fig. 2 the microcanonical entropy per monomer $s(e) = N^{-1}\ln(g(e))$ as a function of the energy per monomer $e = E/N$. It shows the characteristic microcanonical features of a transition with phase coexistence in a small system. For energies right below $e_{\text{ads}}$, the system is in the adsorbed phase AE2 (cf. Fig. 1), i.e., the polymer is in contact with the substrate, but monomer–monomer contacts are not particularly favored and thus expanded conformations dominate. For energies between $e_{\text{ads}}$ and $e_{\text{des}}$, the system is in the transition region, where $s(e)$ is convex. This is clearly seen by constructing the Gibbs hull
\begin{equation}
   H_f(e) = s(e_{\text{ads}}) + e(\partial s/\partial e)_{e = e_{\text{ads}}} - e_{\text{ads}}
\end{equation}
as the tangent that touches $s(e_{\text{ads}})$ and $s(e_{\text{des}})$. Thus,
\begin{equation}
   T_{\text{ads}} = \left(\frac{\partial H_f}{\partial e}\right)^{-1} = \left(\frac{\partial s}{\partial e}\right)^{-1} e = e_{\text{ads}}
\end{equation}
is the microcanonical definition of the adsorption temperature, which coincides with the temperature determined in canonical simulations by the frequently employed criterion of two equal-height peaks in the energy distribution.40 However, due to the convex well of $s(e)$, the definition of a single transition temperature is misleading; the transition rather spans a region of temperatures. Equivalently, for small systems in the canonical ensemble, fluctuation maxima or two equal-weight peaks are located at different temperatures30 which also renders the definition of a unique transition temperature impossible. This is obvious for finite systems like proteins, where the thermodynamic limit is unreachable.51 A unique definition of the transition point is in general only possible in the thermodynamic limit.

Let us define the deviation between $s(e)$ and $H_f(e)$ by
\begin{equation}
   \Delta s(e) = H_f(e) - s(e).
\end{equation}
Then, the surface (or interfacial) entropy, which represents the entropic barrier of the two-state transition, is defined as the maximum deviation
\begin{equation}
   \Delta_{\text{surf}}q = \max\{\Delta s(e)e_{\text{ads}} \leq e \leq e_{\text{des}}\}.
\end{equation}
The peak is located at $e = e_{\text{sep}}$ and defines the energetic phase-separation point. Finally, the energetic gap between the two macrostates is the latent heat per monomer,
\begin{equation}
   \Delta q = e_{\text{des}} - e_{\text{ads}} = T_{\text{ads}}[s(e_{\text{ads}}) - s(e_{\text{des}})].
\end{equation}
In the thermodynamic limit, a first-order phase transition will be characterized as usual by $\lim_{N \to \infty} \Delta q = \text{const} > 0$, whereas $\lim_{N \to \infty} \Delta s = 0$. The thermodynamic limit is unreachable.51 A unique definition of the transition point is in general only possible in the thermodynamic limit.

3 Results

3.1 Dependence on the surface attraction strength

In Fig. 3(a), the microcanonical entropy $s(e)$ is shown for a 20mer, parametrized by the surface attraction strength $e_a$. Since the high-energy regime is dominated by desorbed conformations, the density of states and hence $s(e)$ are hardly affected by changing the values of $e_a$. The low-energy tail, on the other hand, increases significantly with $e_a$. Thus, it is useful to split the density of states into the contributions of desorbed and adsorbed conformations, $g_{\text{des}}(e)$ and $g_{\text{ads}}(e)$, respectively, such that $g(e) = g_{\text{des}}(e) + g_{\text{ads}}(e)$ and $s_{\text{des,ads}}(e) = N^{-1}\ln g_{\text{des,ads}}(e)$.

We define the polymer to be adsorbed if its total surface energy is $E_{\text{surf}} \approx -0.1e_aN$. Since $s_{\text{des}}(e)$ corresponds to $s_{\text{des,ads}}(e)$, for $e_a > 0$ only the $s_{\text{ads}}(e)$ curves were added in Fig. 3(a). Both, $s_{\text{ads}}(e)$ and $s_{\text{des}}(e)$, are concave in the whole energy range of the adsorption transition. Thus, convex entropic monotony can only occur in the most sensitive region where adsorbed and desorbed conformations have equal entropic weight, i.e., at the entropic transition point. Note that for a polymer grafted at the substrate the translational entropy would be very small. The thus far less pronounced increase of $s_{\text{des}}(e)$ at the entropic transition point is not sufficient to induce the convex intrusion and no microcanonical peculiarities appear in this case.
To transition from desorbed globules (DG) to adsorbed globules (AG), the first scenario corresponds to the docking/wetting (AE2). For larger values of $e_s$, phase coexistence is apparent for the transition between DE and AE2. Here, the corresponding deviations $\Delta e$ from the Gibbs hulls, as plotted in Fig. 3(b), become maximal at the crossing point. The curves of the inverse microcanonical temperatures decrease [i.e., $T^{-1}$ as plotted in Fig. 3(c)] with increasing energy in the transition region. The temperature “bends back”, i.e., in the desorption process from AE2 to DE, the system is cooled while energy is increased. This is a characteristic feature of first-order-like transition behavior of a finite system (called the “backbending effect”) and has also been observed in numerous other systems, such as, e.g., peptide aggregation.

Depending on $e_s$ and thus on the energetic location of the crossing point, the adsorption transition appears to be second-order-like ($\Delta T = 0$ for $e_s \leq 2$) or first-order-like ($\Delta T > 0$ for $e_s \geq 2$) for a finite, noncovalently grafted chain. Referring to the phase diagram in Fig. 1, the first scenario corresponds to the docking/wetting transition from desorbed globules (DG) to adsorbed globules (AG). The $T^{-1}(e)$ curves for $e_s = 0.1$ in Fig. 3(c) do not exhibit microcanonical signatures for a first-order-like character of the adsorption transition which occurs for $e_s = 1$, e.g., near $T_{ads} \approx 0.7$ (see Fig. 1). Noticeably, the inflection points near $T_{ads} \approx 0.77$ ($T_{ads} \approx 1.3$) indicate the $\Theta$-transition that separates coil-like and globular conformations in the bulk (DE/DG). It is a surprising observation that the adsorption transition becomes first-order-like at the point where it falls together with the $\Theta$-transition ($e_s \approx 1.8$, $T \approx 1.3$). This is signaled by the saddle point of the corresponding $T^{-1}$ curve in Fig. 3(c).

### 3.2 Chain-length dependence

Since the adsorption transition between DE and AE2 is expected to be of second order in the thermodynamic limit, first-order signatures found for the finite system must disappear for the infinitely large system $N \to \infty$. Therefore, we now investigate the chain-length dependence of the microcanonical effects. Figure 4(a) shows the microcanonical entropies $s(e)$, the adsorption entropies $s_{ads}(e)$, and the desorption entropies $s_{des}(e)$ for chain lengths $N = 10, \ldots, 40$. The respective slopes of $s_{ads}(e)$ and $s_{des}(e)$ near the crossing points converge to each other with increasing chain length. Hence, the depth of the convex well is getting smaller and thus also the surface entropy decreases [Fig. 4(b)]. Interestingly, the separation energies $e_{sep} \approx -0.95$ [which corresponds to the maxima of $\Delta T$ in Fig. 4(b)] and approximately to the location of the intersection points of $s_{ads}(e)$ and $s_{des}(e)$ in Fig. 4(a) do not depend noticeably on $N$. The desorption energies $e_{des}$ move a little, but the adsorption energies $e_{ads}$ shift much more rapidly towards the separation point, i.e., the latent heat decreases with increasing chain length. Consequently, in Fig. 4(c), the backbending of the (reciprocal) caloric temperatures is getting weaker; the adsorption temperatures converge towards a constant. Note that the microcanonical temperature of these finitely long chains is negative in the high-energy region. This is another characteristic feature of finite systems in the microcanonical analysis and disappears with increasing chain lengths, as can be seen in Fig. 4(c).

For larger values of $e_s$, phase coexistence is apparent for the transition between DE and AE2. Here, the corresponding deviations $\Delta e$ from the Gibbs hulls, as plotted in Fig. 3(b), become maximal at the crossing point. The curves of the inverse microcanonical temperatures decrease [i.e., $T^{-1}$ as plotted in Fig. 3(c)] with increasing energy in the transition region. The temperature “bends back”, i.e., in the desorption process from AE2 to DE, the system is cooled while energy is increased. This is a characteristic feature of first-order-like transition behavior of a finite system (called the “backbending effect”) and has also been observed in numerous other systems, such as, e.g., peptide aggregation.

Fig. 3  (a) Microcanonical entropies and their fraction for adsorbed conformations $s_{ads}(e)$ at various surface attraction strengths $e_s = 0, 1, \ldots, 6$ for a 10mer [the fraction of desorbed structures corresponds to $s(e)$ for $e_s = 0$]; (b) deviations $\Delta s(e)$ from the respective Gibbs hulls (not shown) to illustrate the increase of the surface entropy $\Delta s_{surf}$ and the latent heat $\Delta q$ with the attraction strength $e_s$. Note that $\Delta s_{surf} = \Delta q = 0$ for $e_s = 0, 1$; (c) caloric inverse temperature curves $T^{-1}(e)$ and Maxwell lines at respective reciprocal transition temperatures $T_{ads}$. This journal is © the Owner Societies 2010 Phys. Chem. Chem. Phys., 2010, 12, 11548–11554 | 11551
for larger chains. The rapid decreases of latent heat and surface entropy qualitatively indicate that the adsorption transition of expanded polymers (DE to AE2) crosses over from bimodal first-order-like behavior towards a second-order phase transition in the thermodynamic limit.

In Fig. 5, the chain-length dependences of the surface entropies $D_{\text{surf}}$ and of the latent heats $D_q$ are plotted, parametrized by the surface attraction strength $\varepsilon_s$. The chains considered in our study are too short for a detailed finite-size scaling analysis. However, for $\varepsilon_s > 2$, the plots suggest a power-law dependence of these quantities in this regime. A simple scaling ansatz for the surface entropy is $D_{\text{surf}} \sim N^{-\kappa_s}$, while for the latent heat that trivially scales with $\varepsilon_s$, we choose $D_q/\varepsilon_s \sim N^{-\kappa_q}$. The least-square fits to the data yield

$$\kappa_s = 1.65(1.36,1.24,1.17)$$

and

$$\kappa_q = 0.39(0.37,0.37,0.36)$$

for $\varepsilon_s = 3(4,5,6)$. The fit curves are also inserted into Fig. 5. The fit results for the exponents depend on $\varepsilon_s$ but seem to converge to constant positive values for $\varepsilon_s \rightarrow \infty$. The surface entropy vanishes in the thermodynamic limit independently of the transition characteristics. However, that our data suggest

$$\lim_{N \rightarrow \infty} D_q = 0$$

is support for the assumption of the second-order nature of the adsorption transition. This is consistent with results discussed in ref. 14.

3.3 Variation of the box size

Finally, after noticing that there is a considerable influence of the simulation box size on the microcanonical properties of the adsorption transition, we also want to investigate this effect in more detail. To this end, simulations with $\varepsilon_s = 5$ for a fixed chain length ($N = 20$) were performed for different distances $L_z$ of the steric wall to the attractive substrate. Note that fixing the chain length $N$, but changing $L_z$ will also change the density. Hence, the limit of $L_z \rightarrow \infty$ considered in the following does not correspond to the thermodynamic limit. Analogously to Figs. 3 and 4, the corresponding microcanonical results are displayed in Fig. 6. Because the number of adsorbed conformations cannot depend on the amount of space available far away from the substrate, the unknown additive constants to $s(e)$, $s_{\text{ads}}(e)$, and $s_{\text{des}}(e)$ are chosen in such a way that $s_{\text{ads}}(e)$ coincides for all $L_z$ in Fig. 6(a). It is also possible to
first-order-like character in this limit. The entropic barrier can grow arbitrarily large for large simulation boxes since the part of the phase space in proximity of the attractive substrate gets arbitrarily small. It is interesting to note here that in simulations of the grafted case no intruder was observed.

The resultant caloric inverse temperature curves $T^{-1}(e)$ in Fig. 6(c) only differ in the energy regime, where both entropic contributions, $s_{\text{ads}}(e)$ and $s_{\text{des}}(e)$, are of the same order of magnitude—the coexistence region. Once again, the effect of the intruder gets enhanced with $L_z$ and only in this regime $T^{-1}(e)$ changes with $L_z$. In Fig. 6(c), also the Maxwell lines representing the adsorption temperatures are shown.

One can use the knowledge of the behavior of $s_{\text{ads}}(e)$ and $s_{\text{des}}(e)$ to venture a simple estimate of $T_{\text{ads}}$ by performing a Gibbs construction. In the adsorption phase, the contact point of the Gibbs hull is independent of $L_z$.

$$s(e_{\text{ads}}) = s_{\text{trans}}(e_{\text{ads}}) + s_{\text{conf}}(e_{\text{ads}}).$$

where $s_{\text{trans}}(e_{\text{ads}})$ is the translational entropy parallel to the substrate and $s_{\text{conf}}(e_{\text{ads}})$ the conformational entropy of the adsorbed conformations. The other contact point

$$s(e_{\text{des}}, L_z) = s_{\text{trans}}(e_{\text{des}}, L_z) + s_{\text{trans}}(e_{\text{des}}) + s_{\text{conf}}(e_{\text{des}}),$$

corresponding to the entropy in the desorption phase, is a decomposition of the $L_z$-dependent translational entropy $s_{\text{trans}}(e_{\text{des}}, L_z) = N^{-1} \ln L_z$ and the $L_z$-independent contributions from the translation parallel to the substrate $s_{\text{trans}}(e_{\text{des}})$ and the conformational entropy $s_{\text{conf}}(e_{\text{des}})$. The adsorption temperature is obtained as the inverse slope of the Gibbs hull

$$T_{\text{ads}} = \frac{e_{\text{des}} - e_{\text{ads}}}{s(e_{\text{des}}, L_z) - s(e_{\text{ads}})}$$

The conformational entropies and $\Delta q$ also contain an $N$-dependence, but since we fixed $N$ this is of no interest here.

For practical purposes, relation (13) allows one to restrict oneself to perform a single simulation within a sufficiently large and finite box, and one only has to keep in mind the simple $\ln(L_z)$ dependence on the simulation box size perpendicular to the substrate.

4 Summary

In our multicanonical Monte Carlo simulation study, we have investigated the adsorption transition of polymers at attractive substrates with different binding strengths by means of micro-canonical analyses. For short polymers our analysis revealed that at the adsorption transition temperature, which is here defined by a Maxwell construction, adsorbed and desorbed conformations coexist. This supports the first-order character of this transition for short polymers. The energetic separation of these conformational phases is an estimate for the latent heat which is, in principle, measurable in experiments. Thus, beside the systematic qualitative investigation of the nature of the conformational transitions, the microcanonical analysis also enables quantitative predictions.
We have studied in detail how the character of the conformational transitions depends on the surface attraction strength, chain length, and concentration. It turned out that the stronger the polymer is attracted by the substrate, the larger is the separation of the adsorption and desorption phases and the higher is the surface-entropic barrier, i.e., the first-order character of the adsorption transition strengthens. This is also found if the accessible volume is increased, in which case primarily the translational entropy perpendicular to the substrate controls the surface entropy. However, if the monomer density is kept fixed, but the chain length is increased, surface entropy and latent heat vanish and the transition crosses over into a second-order phase transition in the thermodynamic limit, as expected. We performed scaling analyses for the decrease of these quantities and found them to decay slower for larger surface attraction strengths.

To conclude, our study has shown the usefulness of the microcanonical interpretation of the adsorption transition of nongrafted polymers in the regime of the polymer–substrate phase diagram \(^1\) that is dominated by expanded conformations. This is substantial for the understanding of thermodynamic properties in deposition and self-assembly processes of short polymers or peptides at attractive substrates in good solvent. In particular, the discovery of substrate and sequence specificities in the binding of small proteins at semiconductor substrates,\(^8\)–\(^13\) with potential for nanotechnological applications, has renewed the interest in and manifested the need of a more fundamental and systematic investigation of adsorption transitions.

Acknowledgements

This work is partially supported by the DFG (German Science Foundation) within the Graduate School BuildMoNa and under Grant Nos. JA 483/24-1/2/3, the Deutsch-Französische Hochschule (DFH-UFA) under Grant No. CDFA-02-07, and by the German-Israel Program “Umbrella” under Grant No. SIM6. Support by supercomputer time grants (Grant Nos. hlz11 and jiff39) of the Forschungszentrum Jülich are gratefully acknowledged.

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