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The qualitative solvent- and temperature-dependent conformational behavior of a peptide in
the proximity of solid substrates with different adsorption properties is investigated by means
of a simple lattice model. The resulting pseudophase diagrams exhibit a complex structure,
which can be understood by analysing the minima of the free-energy landscape in dependence
of appropriate system parameters.

1 Introduction

The interest in understanding adsorption of polymers and peptides to inorganic material
has grown recently with the development of nanotechnological equipment that enables
present and future applications ranging from nanoelectronic devices [as, for example, the
celebrated organic light-emitting diodes (OLEDs)] to pattern-recognising nanosensors in
biomedicine. In recent experiments, evidence for substrate specificity of synthetic peptide
adsorption to semiconductor substrates has been found.[1] The investigation of organic-
inorganic interfaces is connected with the substantial problem of setting up an effective
microscopic model for the adsorption of organic to inorganic matter in addition to the
intrinsic interactions governing the folding properties of the organic substance. Van der
Waals based interaction models[2] were employed, e.g., in studies of gold-binding pep-
tides.[3] Here, we study a minimalistic lattice model, where the folding part is governed
by the hydrophobic-polar (HP) model,[4] and the interaction with the substrate is restricted
to monomer-type dependent surface-layer attraction.[5, 6]

2 Conformational Transitions in a Simple Hybrid Interface Model

Based on the assumption that peptide folding is mainly due to the hydrophobic effect, we
distinguish only hydrophobic (H) and polar residues (P). According to the minimalistic
HP model[4], the intramolecular energy of a conformation is related to the number of hy-
drophobic nearest-neighbor contacts n_{HH}. For the study of specificity of surface–binding,
we investigate three attractive substrate models: (a) type-independent attractive, (b) hy-
drophobic, and (c) polar substrate. In case (a), the energy of the system is proportional to
the total number of monomer–surface contacts, $n_s^{\mathrm{H+P}}$, while in the cases (b) and (c) the re-
spective hydrophobic (n_s^{H}) and polar (n_s^{P}) surface contacts are energetically favored. The
generic model can be defined by $E(n_s, n_{\mathrm{HH}}) = -n_s - s n_{\mathrm{HH}}$, where, depending on the
substrate model, $n_s = n_s^{\mathrm{H+P}}$, n_s^{H}, or n_s^{P}. The parameter s controls the solvent quality (the
larger the value of s, the worse the solvent). The contact numbers n_s and n_{HH} are natural
system parameters that allow the discrimination of conformational pseudophases. In our
investigations of this system, we employed the contact-density chain-growth method which
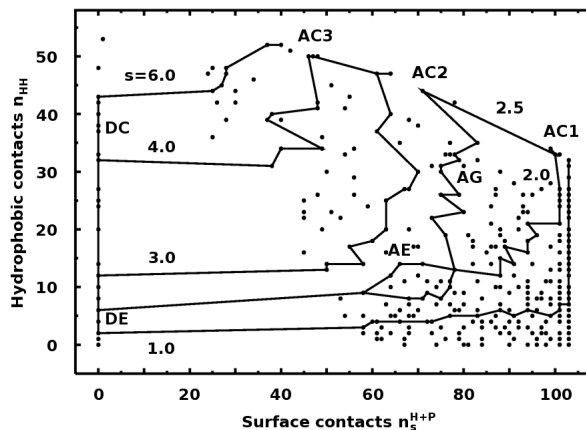
Figure 1. Contact-number map of all free-energy minima for an exemplified peptide with 103 monomers[5] and a substrate which is equally attractive to all monomers. Circles correspond to minima of the contact free energy $F_{T,s}(n_s^{H+P}, n_{HH})$ in the parameter space $T \in [0, 10]$, $s \in [-2, 10]$. Lines illustrate how the contact free energy changes with the temperature at constant values of the solvent parameter s.

has successfully been applied in adsorption studies of polymers.[8] This method, which is a suitably generalized variant of the multicanonical chain-growth algorithm,[7] allows us to estimate the contact density $g(n_s, n_{HH})$, which simply counts the number of conformations for a given pair of contact numbers n_s and n_{HH}. For fixed temperature T and solubility s, we define the contact free energy $F_{T,s}(n_s, n_{HH}) \sim -T \ln g(n_s, n_{HH}) \exp(-E_s/T)$. Assuming that the minimum of the free-energy landscape $F_{T,s}(n_s^{(0)}, n_{HH}^{(0)})$ is related to the class of macrostates with $n_s^{(0)}$ surface and $n_{HH}^{(0)}$ hydrophobic contacts, this class dominates the pseudophase the system resides in. For this reason, it is instructive to calculate all minima of the contact free energy and to determine the associated contact numbers in a wide range of values for the external parameters. This can easily be done with the knowledge of $g(n_s, n_{HH})$ by simple reweighting.

In Fig. 1, the map of all possible free-energy minima (circles) in the range of external parameters $T \in [0, 10]$ and $s \in [-2, 10]$ is shown for a peptide with 103 monomers (37 hydrophobic, 66 polar) in the vicinity of a substrate that is equally attractive for both hydrophobic and polar monomers.[5, 6] There are a few regions of circles which can be associated with pseudophases. Clearly, where the number of surface contacts n_s^{H+P} is zero, the heteropolymer is desorbed and in the bulk regime two main pseudophases can be identified: desorbed extended (DE) and desorbed collapsed (DC) hydrophobic-core conformations. In case of adsorption, we distinguish also extended (AE) and compact (AC1-3) conformations, and an intermediate globular pseudophase (AG), where conformations are globally compact, but do not exhibit pronounced hydrophobic domains. The discrimination of the three AC subphases is due to layering: In dependence of the solvent quality, hydrophobic domains form layers: single-layer domains in AC1 (good solvent, substrate contact favored prior formation of intrinsic hydrophobic contacts), and respective hydrophobic double- and triple-layer cores in AC2 and AC3. Solid lines in Fig. 1 visualize "paths" through the

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free-energy landscape when changing temperature, but leaving the solvent parameter unchanged ($s = \text{const}$). Recalling that larger s values correspond to worse quality of the solvent, it is obvious that the $s = 6$ path at low temperatures starts in the highly compact AC3 subphase. Increasing the temperature, the monomers reorder and the system enters for entropic reasons the globular pseudophase AG. Approaching $T \approx 2.3$ a noticeable first-order-like unbinding transition occurs towards pseudophase DC, before the compact structure decays (DE). Under very good solvent conditions as, e.g., for the trajectory of $s = 1$, the favored conformations at low temperatures are film-like. Increasing the temperature slightly to $T \approx 0.2$, the system crosses over to the AE pseudophase. This subphase is very stable under these solvent conditions, but close to $T \approx 2.3$ the heteropolymer desorbs into the dissolved bulk phase DE.

For the other two substrates, the pseudophase diagrams look quantitatively different but most of the main pseudophases are also present in these cases.[5]

3   Concluding Remarks

Beside the expected adsorbed and desorbed phases, hybrid organic-inorganic systems exhibit a rich subphase structure in the adsorbed phases with compact hydrophobic domains. In this region, the binding behavior is strongly substrate-specific and depends in detail on the quality of the solvent. Since current experimental equipment can reveal molecular structures at the nanometer scale, it should be possible to investigate the grafted structures in dependence of the solvent quality. Such experiments would be essential for studies of binding forces that are strong enough to refold peptides or proteins.

Acknowledgments

References

1. S. R. Whaley, D. S. English, E. L. Hu, P. F. Barbara, and A. M. Belcher, Nature (London) **405**, 665 (2000); K. Goede, P. Busch, and M. Grundmann, Nano Lett. **4**, 2115 (2004).
2. R. Hentschke, Macromol. Theory Simul. **6**, 287 (1997).
3. R. Braun, M. Sarikaya, and K. Schulten, J. Biomater. Sci. Polym. Ed. **13**, 747 (2002).
4. K. A. Dill, Biochemistry **24**, 1501 (1985).
5. M. Bachmann and W. Janke, Phys. Rev. E **73**, 020901(R) (2006);
6. M. Bachmann and W. Janke, *Chain-growth simulations of lattice-peptide adsorption to attractive substrates*, in: Proceedings of the NIC Symposium 2006, John von Neumann Institute for Computing, Jülich, NIC Series vol. **32**, ed. by G. Münster, D. Wolf, M. Kremer (NIC, Jülich, 2006), p. 245.
7. M. Bachmann and W. Janke, Phys. Rev. Lett. **91**, 208105 (2003).
8. M. Bachmann and W. Janke, Phys. Rev. Lett. **95**, 058102 (2005); Phys. Rev. E **73**, 041802 (2006).