

Chapter 2

Particle-Based Models of Organic Semiconductors

A core challenge in computational materials science is the prediction of materials properties from first principles and hence—in the context of molecular materials—from input chemical structures. In this chapter, we present a workflow for particle-based microscopic simulations of organic semiconductors that aims to achieve just that. It is tailored to the description of non-adiabatic charge transport. The workflow can be broken down into three steps: First, the material morphology is simulated at an atomistic level, using molecular dynamics or other particle-based models, including coarse-graining and backmapping techniques. Second, a charge transport network is constructed from the simulated morphology, built on a rate-based description, where the parametrization of the rates is achieved on a quantum or quantum-classical level. Third, kinetic Monte-Carlo simulations are used to derive macroscopic observables, notably charge-carrier mobilities, or simulate current-voltage characteristics of realistic devices either directly or via parametrization of continuous drift-diffusion models.

2.1 The Bottom-Up Simulation Workflow

The functional properties of organic semiconductors arise from structural features and dynamic processes across many length and time scales. On the structure side, local molecular packing (10^{-9} m), domain organization (10^{-8} m) and device-level architecture (10^{-7} m) all have an impact on device characteristics. The same applies to the time domain: Nuclear vibrations (10^{-15} s), charge transfer dynamics (10^{-15} – 10^{-9} s), molecular diffusion (10^{-9} s) and charge migration (10^{-9} – 10^{-6} s) necessitate a similarly *multiscale* picture. With today's computational resources, there is no simulation technique available that can possibly address all these length

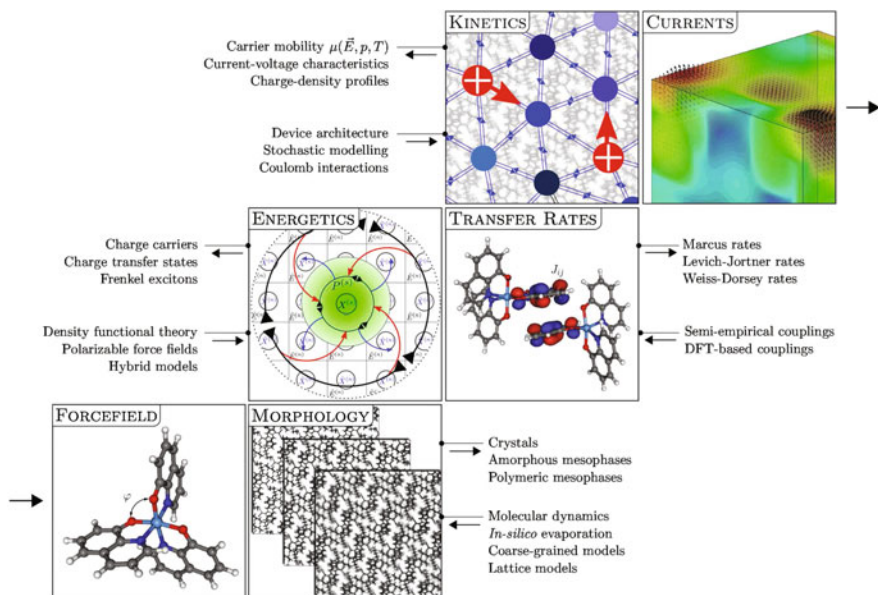


Fig. 2.1 Bottom-up workflow for charge and energy transport simulations. The schematic summarizes the three-level procedure as implemented in the VOTCA software suite. Bottom: particle-based simulation of the material morphology via force-field-based molecular dynamics, including atomistic, coarse-grained or lattice models. Centre: partitioning of the morphology onto a transport network and parametrization thereof from first principles. Top: simulation of kinetics on the charge transport network and evaluation of macroscopic mobilities and currents

and time scales simultaneously. For practical computations, approximations based on a separation of these scales are inevitable.

In organic semiconductors (and soft matter in general) an at least partial separation of time and length scales derives from the difference in strength of the interactions between and within the molecular building blocks—different from most “hard” matter, where the extended conjugated network in inorganic semiconductors or long-range metallic binding in metals prevent any such distinction. For the problem of charge transport in organic materials, the weak intermolecular coupling implies that nuclear and electronic degrees of freedom can (to some approximation [1–3]) be decoupled in a *small-polaron* way: Intramolecular nuclear/vibrational degrees of freedom are then included effectively in an appropriately chosen rate expression for charge or energy transfer, such as the semi-classical Marcus rate. Molecular diffusion, on the other hand, can be entirely disentangled from the dynamics of electronic states. Electronic processes are hence thought to occur in a *frozen* morphology that can be precomputed.

Figure 2.1 presents the simulation workflow associated with this separation of time scales. In the following sections of this chapter, we will work our way through the individual stages of the workflow (except for the energetics of excitations, to which we

devote a separate chapter). The nutshell version reads as follows: First, the material morphology is simulated based on atomistic or coarse-grained force fields. This may include particle-based methods with phenomenological interactions required to address morphological scales beyond the limit set by atomistic molecular dynamics. A significant fraction of the complexity of organic materials enters at this stage due to the diverse structuring of materials, ranging from crystalline to liquid-crystalline to amorphous ordering and including domain and interface formation, grain boundaries, binary mixtures, electrodes, etc. Once the morphology has been simulated, a transport network is generated from the molecular landscapes and the associated reaction rates parametrized from first-principles-based techniques. Already at this stage, structure-property relationships that relate morphological features to the energy landscape (as the focal point of this work) can be established. Finally, dynamics on the network can be simulated to evaluate charge-carrier or exciton mobilities, which can be further used in device simulations built on larger stochastically generated transport networks or continuous device models.

The outlined simulation protocol, which is by now routinely used for the study of charge transport in organic semiconductors, is implemented in the open-source simulation package VOTCA (Versatile Object-oriented Toolkit for Coarse-graining Applications) [4]. The modular structure of this toolkit—whose extension was an important aspect of this work—includes four sub-libraries, each devoted to a specific task in the workflow from Fig. 2.1: The coarse-graining library VOTCA::CSG allows the derivation of coarse-grained potentials for the morphology simulation. The charge-transport module VOTCA::CTP assists with the generation of the transport network and parametrization of the transfer rates, including the computation of energies of electronic states (charge carriers, charge transfer states, Frenkel excitons) and the calculation of electronic couplings. The molecular orbital overlap library VOTCA::MOO implements a semi-empirical ZINDO approach tailored to the computation of these couplings in large systems. Finally, the VOTCA::KMC module incorporates a kinetic Monte Carlo code that simulates dynamics on the generated transport network.

2.2 Molecular Landscapes

The morphological complexity of the molecular and polymeric solid state (characteristic of many soft matter systems) renders a unified description infeasible. Still, there are a range of computational approaches available to describe at least select features of the morphology associated with different length and time scales (see our introductory discussion). Here, we will focus on particle-based descriptions targeting system sizes up to 100 nm, where “particles” may represent nuclei and electrons, atoms, molecular moieties or entire molecules. These should be contrasted with field-based descriptions, notably classical density functional theory based, e.g., on time-dependent Ginzburg-Landau theory. Field-based approaches are, however, less suited for charge and energy transport simulations, which rely on an atomistic

representation of the system, obtained from particle-based methods either directly or after backmapping.

In the following, we will describe how particle-based descriptions at different levels of resolution are employed to obtain realistic microscopic models of organic semiconductors. Figure 2.2 presents an overview over the thus obtained morphologies, grouped according to system type (bulk, heterojunction, grain boundary) and resolution (atomistic, coarse-grained, lattice). We will begin with the highest level of resolution, and in doing so first introduce two computational techniques widely applied to molecular ordering at the atomistic scale: quantum-mechanical density functional theory and classical molecular dynamics.

2.2.1 Density Functional Theory

Density functional theory (DFT) [5] is a popular approach to study ground-state structural and electronic properties of interacting many-body systems. The underlying idea is to absorb the interaction between the particles into an energy functional of the particle density, leading to an effective description of the system in terms of non-interacting particles—thus reducing computational complexity. Quantum-mechanical DFT targets the interacting-particle problem described by a Hamiltonian of the form [6]

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \\ & - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}. \end{aligned} \quad (2.1)$$

with nuclei at positions $\mathbf{R} = \{\mathbf{R}_I\}$, with charges $\mathbf{Z} = \{Z_I e\}$ and masses $\mathbf{M} = \{M_I\}$, and electronic coordinates $\mathbf{r} = \{\mathbf{r}_i\}$. The challenge in solving the Schrödinger equation for the above Hamiltonian is primarily due to the electron-electron repulsion term, i.e., the third term on the right-hand side of Eq. 2.1. The Coulomb interaction between electrons gives rise to quantum-mechanical exchange and correlation. Exchange phenomena can still be captured with a many-body wave function in the form of a single Slater determinant used in Hartree-Fock, whereas correlation effects, which further lower the energy of the system, require at least linear combinations of these determinants (leading to the Configuration Interaction approach). To avoid the computational difficulties associated with this complicated many-body wave function, the Kohn-Sham construction of DFT operates on an effective energy functional of the electron density ρ ,

$$U[\rho] = T[\rho] + \int V_{\text{ext}}(\mathbf{x}) \rho(\mathbf{x}) d^3x + \int \frac{\rho(\mathbf{x}) \rho(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x d^3x' + U_{\text{xc}}[\rho], \quad (2.2)$$

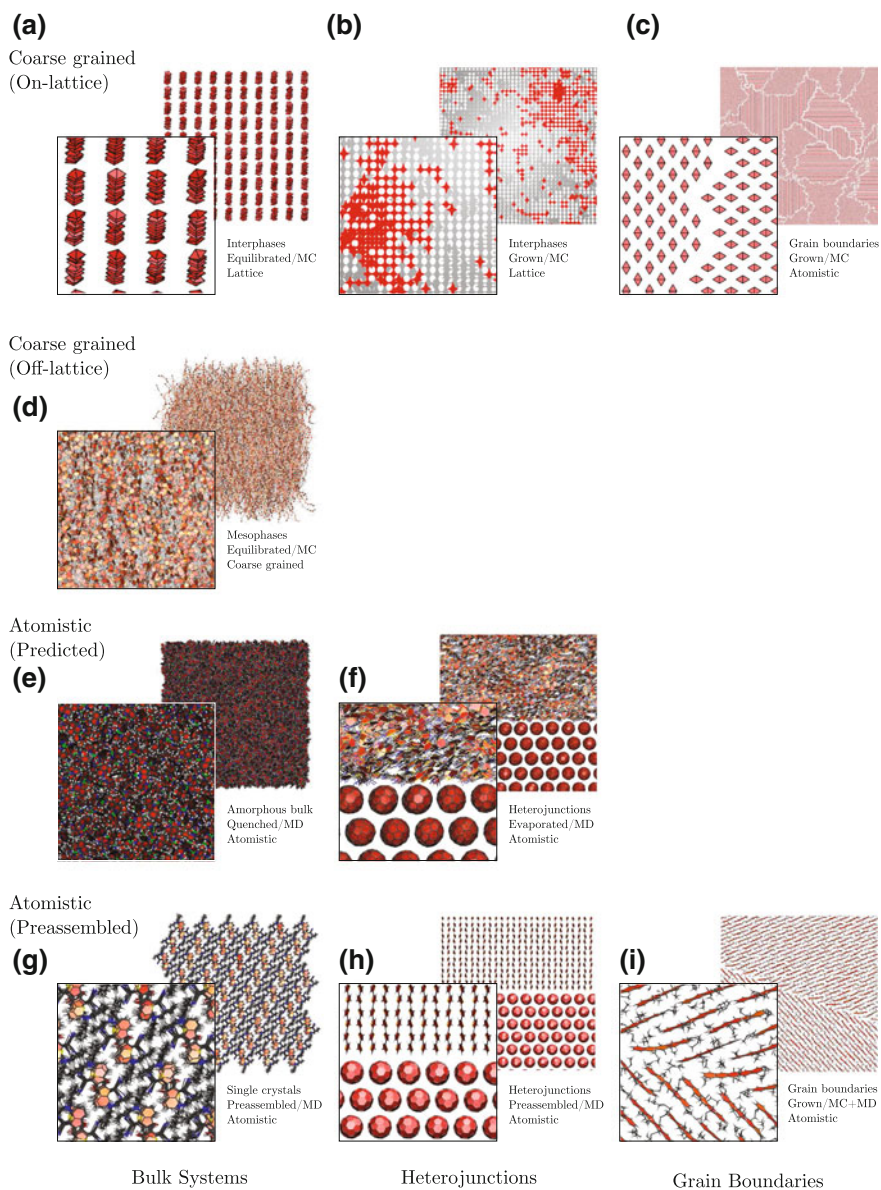


Fig. 2.2 Bulk and interfacial morphologies. Overview over lattice (a–c), coarse-grained (d) and atomistic (e–i) models of organic semiconductors studied in this work, classified according to system type (bulk, heterojunction, grain boundary). In the visualizations, π -conjugated rings are represented by red polygons

with $T[\rho]$, the kinetic energy of the non-interacting effective particles, the nuclear-attraction potential $V_{\text{ext}}(\mathbf{x})$, the classical Hartree (self-)energy of the charge density with associated potential $V_H(\mathbf{x})$, and finally the exchange-correlation functional $U_{\text{xc}}[\rho]$. The ground-state particle density follows from a variational principle: Based on the functional from Eq. 2.2, the Kohn-Sham eigenvalue equations result as

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{ext}}(\mathbf{x}) + V_H(\mathbf{x}) + \frac{\delta U_{\text{xc}}}{\delta \rho} \right] \varphi_i^\sigma(\mathbf{x}) = \varepsilon_i^\sigma \varphi_i^\sigma(\mathbf{x}). \quad (2.3)$$

For computational convenience, the particle density ρ is expanded in terms of single-electron orbitals (basis functions) of spin σ , $\varphi_i^\sigma(\mathbf{x})$:

$$\rho(\mathbf{x}) = \sum_{i=1}^N \sum_{\sigma} |\varphi_i^\sigma(\mathbf{x})|^2. \quad (2.4)$$

Starting from an initial guess for the density, Eqs. 2.3 and 2.4 are solved in a self-consistent-field (SCF) manner. The accuracy of the resulting density and energy greatly relies on an appropriate choice for the basis set $\{\varphi_i^\sigma\}$ and the exchange-correlation functional U_{xc} . As the exact form of this functional is only known for the free-electron gas, various parametrizations—tailored to different systems and observables—exist. Within this work, we will use the B3LYP (Becke, three parameters, Lee-Yang-Parr) hybrid functional, which has been parametrized on and shown to accurately describe ground-state energies of molecules, including ionization energies. This hybrid functional combines exact exchange from Hartree-Fock with functionals based on the local density and generalized gradient approximations (LDA and GGA), using three weighting coefficients extracted from fits to reference energies of a large set of molecules.

For the expansion of the density, we will use so-called *split valence triple zeta* basis sets [7] with additional polarization functions, typically denoted in the form $X - Y_1 \dots Y_N g$: 6-311+g(p,d), for example, indicates that core electron orbitals are contracted from six primitive Gaussians, whereas valence atomic orbitals are composed of $N = 3$ basis functions ($Y_1 \dots Y_N = 311$), where the first one is itself a contraction of three primitive Gaussians. Finally, additional (p , d) functions of angular momentum $l = 1$ and $l = 2$, respectively, are added to capture polarization, next to diffuse (+) functions on heavy atoms.

Due to its accuracy and computational efficiency, density functional theory is well suited to study molecular arrangements with a size of on the order of hundreds of atoms. Gas-phase properties, including ionization energies and electron affinities, can hence be calculated with relative ease. In doing so, it should be noted that orbital energies in DFT do not carry physical meaning. Hence, ionization energies and electron affinities should always be computed from two independent calculations on the neutral and charged molecule. As an example, Fig. 2.3 provides a summary of the gas-phase energetics of different DCV5T derivatives obtained by DFT with the B3LYP functional and a small (6–31 g) basis set. Naturally, such calculations in

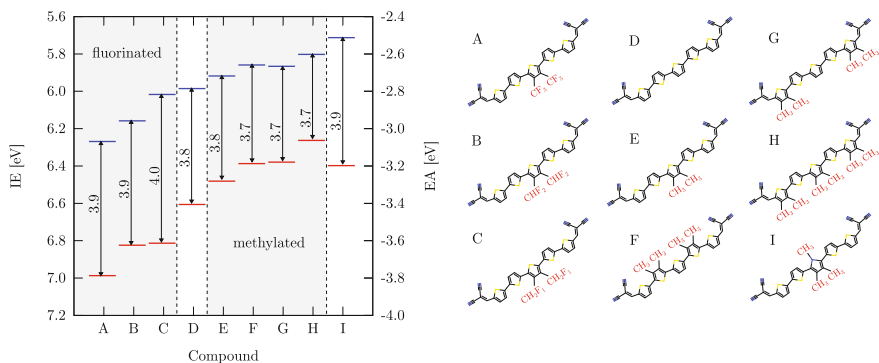


Fig. 2.3 Fluorination versus methylation of DCV5T. Gas-phase ionization energies (IE, red bars with left axis) and electron affinities (EA, blue bars with right axis) for derivatives of the acceptor-substituted oligothiophene DCV5T computed via DFT with the B3LYP functional and 6–31 g basis set. Note that in compound I, the central thiophene is replaced by a pyrrole

gas-phase should not be used to extrapolate to the solid state. Still, they can serve as a first indicator how variation of side chains and functionalization via exchange of chemical moieties may impact energetics, here shown for the case of fluorination and methylation. Specifically, Fig. 2.3 illustrates how attachment of electronegative units (fluoromethyl) lowers the energy of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively), whereas electropositive groups (methyl) effect the opposite.

2.2.2 Molecular Dynamics

Even though DFT accurately describes molecular ground-state electronic and conformational properties, it is not suited to sample the morphology of molecular materials beyond small molecular clusters due to the associated computational complexity. For the simulation of material morphology on the scale of tens of nanometers, classical molecular dynamics (MD) [8] is the method of choice. It relies on a classical parametrization of the potential energy surface of the many-body system, obtained from first principles calculations or experimental data. Based on this *force field*, the Newtonian equations of motions are integrated numerically within a suitably chosen thermodynamic ensemble, using energy-conserving and time-reversible integrators as based, for example, on the leap-frog algorithm:

$$\mathbf{r}_i(t + dt) = \mathbf{r}_i(t) + \mathbf{v}_i(t + dt/2)dt, \quad (2.5)$$

$$\mathbf{v}_i(t + dt/2) = \mathbf{v}_i(t - dt/2) + \mathbf{f}_i(t)/m_i dt. \quad (2.6)$$

Here, $\mathbf{f}_i(t)$ is the force acting on particle i at position $\mathbf{r}_i(t)$ with velocity $\mathbf{v}_i(t)$. The main difference from other sampling techniques, notably Monte-Carlo (MC) approaches, is the explicit time coordinate t along which the dynamics are simulated. Accordingly, MD approximates the ensemble average of a physical observable by its time average rather than an average over (canonically or otherwise sampled) coordinate configurations. Compared to MC, this can result in a lower sampling efficiency, for example in “simple” systems with characteristic, slow relaxation modes, but enables the simulation of non-equilibrium processes where particle velocities (giving, for instance, rise to hydrodynamic flow fields) are relevant descriptors. Furthermore, adaptations of the MD formalism such as stochastic dynamics (SD) can improve the sampling speed via a stochastic force (resembling a friction term) acting on the particles, with its time-correlation adjusted to preserve a canonical ensemble.

Typical ensembles used in MD are of the NVT or NPT type, the former enforcing a constant volume (V), the latter a constant pressure (P) next to conserved particle number (N) and temperature (T). Whereas particle number and system volume can be trivially fixed by the initial configuration and choice of the simulation cell, pressure and temperature control require additional coupling algorithms. The Berendsen barostat [9], for example, subjects the pressure tensor calculated from the atomistic configuration,

$$P = \frac{1}{V} \left(\sum_i m_i \mathbf{v}_i \otimes \mathbf{v}_i + \sum_{i < j} \mathbf{r}_{ij} \otimes \mathbf{F}_{ij} \right), \quad (2.7)$$

to a relaxation law $dP/dt \sim (P_0 - P)/\tau_p$ that links the pressure change dP to a target pressure P_0 according to a relaxation time τ_p . The system compressibility relates this pressure to a volume change. Hence, the pressure relaxation is achieved by simultaneous scaling of the particle positions and simulation cell.

Whereas pressure coupling is most relevant during the initial relaxation phase of a system, temperature coupling is crucial throughout the entire simulation run. Here, despite the classical description, system sizes studied by MD are still insufficient in the sense that the explicit simulation of an appropriately sized heat bath is not only computationally prohibitive, but would furthermore result in large energy fluctuations of the coupled subsystem due to the relatively small number of contained particles (on the order of 10^5 rather than the macroscopically required 10^{23}). To perform simulations at constant temperature that avoid the computational overhead associated with an explicit heat bath and prevent large finite-size-induced fluctuations of the energy, a virtual heat bath (thermostat) is implemented either through direct manipulation of the particle velocity via rescaling or stochastic “kicks”, or through extension of the system Lagrangian by a virtual degree of freedom that transfers energy between an implicit heat bath and the particle system. The SD formalism, for example, already implements a thermostat due to the stochastic friction term, where the coupling strength follows from the chosen friction coefficient. For MD, we will usually resort to the efficient velocity-rescaling algorithm [10] implemented in the MD package GROMACS [11]. Here, the kinetic energy spread out over N_f degrees

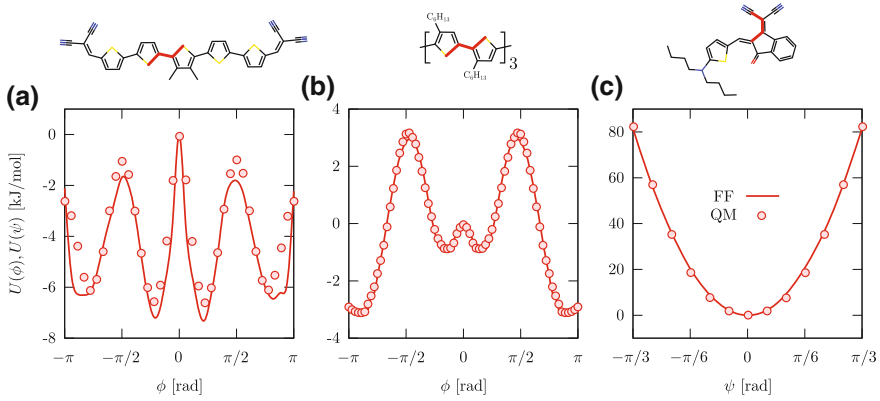


Fig. 2.4 Parametrization of classical force fields. Potential energy surface (PES) resolved along the torsional degrees of freedom as highlighted in the chemical structures of DCV5T (a), P3HT (b) and EL86 (c). The PES in the classical parametrization (solid lines) successfully approximates the reference PES calculated via DFT-B3LYP/6-311+g(d,p) (circles)

of freedom is allowed to fluctuate according to a canonical distribution: The change in kinetic energy for each integration step is subjected to an equation of motion, incorporating both a relaxation term that reverts the kinetic energy to its ensemble average $\frac{1}{2}N_f k_B T$ with a time constant τ , next to a Wiener process inherited from SD.

The quality of MD simulations greatly relies on the accuracy of the underlying force field. This force field features contributions from both bonded (*b*) and non-bonded (*nb*) interactions described by two-, three- and four-body potentials:

$$\mathbf{f}_i = -\nabla_i \left(\sum_{\langle j,k \rangle}^{(nb)} U_{jk}^{nb} + \sum_{\langle j,k \rangle}^{(b)} U_{jk}^b + \sum_{\langle j,k,l \rangle}^{(b)} U_{jkl}^b + \sum_{\langle j,k,l,m \rangle}^{(b)} U_{jklm}^b \right). \quad (2.8)$$

Here, non-bonded interactions absorb the coulombic and van-der-Waals, as well as Pauli exclusion interaction between particles in a pairwise approximation. For the parametrization of these non-bonded interactions, it suffices to specify atomic charge, Lennard-Jones radius σ_i and well-depth ϵ_i , provided the Lennard-Jones potential

$$U_{\text{L}}^{(nb)}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (2.9)$$

is used to model the combined effect of Pauli repulsion ($\sim r^{-12}$) and van-der-Waals attraction ($\sim r^{-6}$) based on the combination rules $\sigma_{ij} = \sqrt{\sigma_i \sigma_j}$ and $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$. Meanwhile, bonded interactions are modelled using bond (two-body), angle (three-body) and dihedral (four-body) potentials including

$$U_{\text{ang}}(\theta) = \frac{1}{2}k_{\theta}(\theta - \theta_0)^2, \quad (2.10)$$

$$U_{\text{imp}}(\psi) = \frac{1}{2}k_{\psi}(\psi - \psi_0)^2, \quad (2.11)$$

$$U_{\text{RB}}(\phi) = \sum_{n=0}^5 C_n \cos^n(\phi). \quad (2.12)$$

Here, U_{RB} is a Ryckaert-Bellemans potential which describes “soft” torsional degrees of freedom ϕ , whereas U_{imp} defines “hard” (improper) dihedrals ψ with a harmonic behaviour throughout the thermally accessible range of motion. For illustration, Fig. 2.4a–c shows potential-energy surface scans associated with the backbone torsional degrees of freedom in three different compounds. The underlying potentials are either of the Ryckaert-Bellemans (Fig. 2.4a, b) or harmonic form (Fig. 2.4c). They were parametrized from reference DFT-B3LYP/6-311+g(d,p) calculations by fitting the difference between the MD and DFT energy, the former calculated with zero force applied to the scanned degree of freedom, to the appropriate expression for the potential.

Note that in developing a force field, the differentiation between bonded and non-bonded interactions on an *intramolecular* level is to some degree ambiguous and has to be set by convention: The OPLS-AA [12] force field, for example, from which we will adopt Lennard-Jones parameters, excludes non-bonded interactions between particles separated by less than three chemical bonds. Particles separated by three bonds experience a potential that is scaled down by a factor 1/2. Only particles separated by more than three bonds are subjected to the full non-bonded potential.

2.2.3 Atomistic Models

We will now present examples for how MD is applied to the study of organic semiconductors. The aim is to develop atomistic models that can subsequently be used for electronic structure calculations. As MD is limited to system sizes of on the order of 10^6 particles and simulation times of 10^{-6} s, atomistic models typically focus on the local molecular packing. The latter may include a basic account of supramolecular features such as a grain boundary or molecular heterojunction.

Within these limits, atomistic simulations are still rarely truly predictive as experimental input and/or physical intuition is required to set up the initial configurations. The problem of molecular self assembly in particular tends to exceed the scope of atomistic simulations due to the slow sampling of the phase space. Techniques used in crystal structure prediction therefore do not access the free energy landscape dynamically, but instead rely on MC-based techniques (notably basin hopping [13]). Even then, the computational cost of structure prediction increases significantly as the conformational properties of the molecular building blocks become more complex, to the degree that a treatment as rigid objects is no longer appropriate. Additionally,

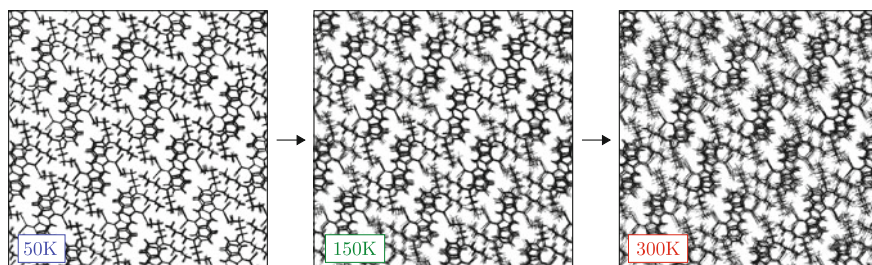


Fig. 2.5 Thermalization of an EL86 crystal via stochastic dynamics. Temperature-induced conformational disorder at $T = 50$ K, 150 K and 300 K in an EL86 supercell assembled and optimized from its experimental X-ray structure. The simulated thermal disorder impacts electronic properties via the broadening of the density of states and thus plays a crucial role in capturing the temperature-dependence of the charge-carrier mobility

computations usually reveal several (local) minima of the energy landscape which are degenerate within the accuracy of the underlying force field. With the “true” minimum found, it still remains to be shown that the thus obtained configuration also corresponds to the minimum of the *free-energy* landscape relevant at finite temperature.

Within this work, we will rely on experimental input structures for crystalline systems where available. These structures, extracted, for example, from X-ray scattering spectra or electron diffraction patterns, are subsequently refined on a force-field level. This optimization has to allow for both the relaxation of nuclear coordinates, in particular the removal of extreme coordinates, and relaxation of the unit cell vectors. This can be achieved via stochastic dynamics with a strong friction coefficient in the *NPT* ensemble at $T = 0$ K. Subsequently, the system is thermalized (see Fig. 2.5) to study its stability and phase behaviour. Of particular interest is the identification of crystal polymorphs, frequently encountered in molecular materials. In some systems, including the polymeric semiconductor P3HT [14], MD simulations can access these different polymorphs, which may differ both structurally and dynamically with respect to backbone and side-chain packing—with interesting implications for charge transport [15].

Different from (poly-)crystalline materials typically used in thin-film transistors and solar cells, OLED compounds only—if at all—display rudimentary molecular ordering. These structures are then accessible through direct simulation based on a randomly generated starting configuration. This independence from experimental input is a considerable advantage for in-silico compound screening.

Beyond this simple, but predictive approach for amorphous bulk systems, in-silico deposition techniques (see Fig. 2.6) sample interfacial ordering at organic heterojunctions without the need for an initial configuration preassembled from experimental input. Still built on atomistic MD, this method may not, however, appropriately address the long relaxation times associated with the self-assembly process. Additionally, as the simulated thin-film growth velocities exceed the exper-

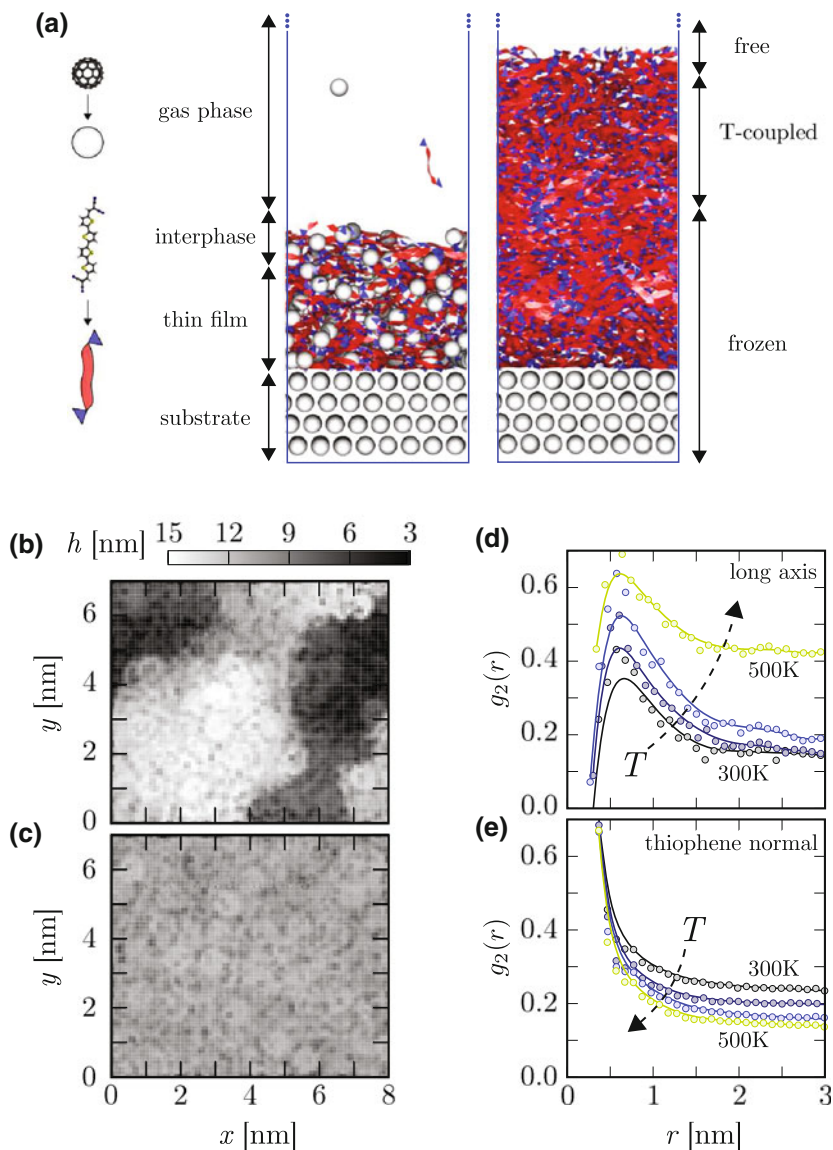


Fig. 2.6 In-silico deposition approach. **a** Molecular dynamics snapshots during the coevaporation of C_{60} :DCV4T (right) and DCV4T evaporation (left) on a C_{60} substrate. In the snapshot, the two molecules are represented in a simplified manner as indicated on the very left. **b,c** Height profiles $h(x, y)$ of the coevaporated system without (**b**) and with (**c**) a linear weighting function $w(x, y) \sim 1/h(x, y)$ for the injection of new molecules above the substrate. **d, e** Orientational correlation function for the pristine DCV4T system for the long molecular axis (**d**) and thiophene normals (**e**) at substrate temperatures of 300 K (black curve), 370 K (dark blue), 440 K (blue) and 500 K (green) after cooling and subsequent equilibration for 5 ns at 300 K

imental deposition speed by many orders of magnitude, artificially induced island growth (see the height profile in Fig. 2.6b) has to be actively prevented through an accelerated surface diffusion. The latter is effectively modelled via a weighting function $w(x, y) \sim 1/h(x, y)$ for molecule insertion that is inversely proportional to the height profile $h(x, y)$ and this way ensures homogeneous thin-film growth (Fig. 2.6c). As a considerable merit of this approach, self-assembly into at least partially ordered supramolecular structures can be accessed. The characterization of these structures proceeds via suitably chosen order parameters and correlation functions that quantify dynamic and/or static properties. Figure 2.6d, e, for example, plots the orientational correlation function

$$g_2(r) = \langle P_2(\cos \theta_{ij}) \rangle_{r_{ij}=r}, \quad (2.13)$$

associated with the long-molecular axis (Fig. 2.6d) and thiophene normals (Fig. 2.6e) of the DCV4T molecule obtained from the analysis of a 12 nm thin film grown on C₆₀. Here, $\langle \dots \rangle$ denotes an ensemble average, $P_2(x)$ is the second-order Legendre polynomial, and θ_{ij} is the angle between the respective directors of molecules i and j at separation r_{ij} in the interval $[r, r + \delta r]$. For DCV4T, the g_2 's indicate that smectic ordering (visually perceptible in Fig. 2.6a) increases, whereas π -stacking decreases with increasing substrate temperature. This liquid-crystalline ordering is simply the effect of the rod-like architecture of the molecules, under the artificially imposed constraint that the smectic layers have to line up periodically. Even though our analysis correctly indicates a face-on orientation of the DCV4T on C₆₀ as the preferred configuration [16], dependable insights into the properties of the *experimental* system are beyond the scope of the approach. Nevertheless, the obtained non-equilibrium structures prove useful to understand the electronic properties of partially-ordered systems, which is indeed how we will make use of them later on in Chaps. 4 and 5.

2.2.4 Coarse-Grained Models

The primary challenge in the simulation of atomistic morphologies results from the slow dynamics that accompany the extremely rugged free-energy landscape to which molecular processes are subjected: These include crystallization, domain formation, the self assembly of the molecular constituents into lamellae or nanofibers, and host-guest interdiffusion.

One way to nevertheless access these processes in simulations, together with the associated length scale of several hundred nanometers, relies on coarse-graining the atomistic degrees of freedom into effective degrees of freedom representing a collection of atoms, entire monomers or even molecules [17]. Such a particle-based coarse-graining approach relies on a separation of time and length scales, where fast time scales and short length scales are implicitly absorbed in the coarse-grained particles described via effective interactions derived from atomistic reference simula-

tions using structure- [18], force- [19] or entropy-based [20] protocols. The achieved computational speed-up is then due, first, to the reduction of explicit degrees of freedom, second, to the reduced friction in the system that follows from a smoothened free-energy surface.

An important application of such approaches targets mesophases of conjugated polymers, characterized by their slow relaxation times and long-range conformational order that ranges from lamellar-crystalline to liquid-crystalline to amorphous within the same material. Conventional coarse-graining techniques using isotropic interaction potentials for conjugated moieties are in this case insufficient as they disregard the anisotropic character of the π - π interactions that drive biaxial backbone ordering [21–25].

In the following, we will introduce a soft coarse-grained model designed to capture these interactions on a phenomenological level, while preserving enough microscopic detail to allow for reinsertion of atomistic details. The model and backmapping scheme were developed by P. Gemünden and K. Daoulas [26]: Within the model, particles represent entire repeat units of the polymer, including side chains. The local frame of these particles is given by the right-handed trihedron $\{\mathbf{u}, \mathbf{v}, \mathbf{w}\}$, where $\mathbf{u}$ points along the backbone, $\mathbf{w}$ along the normal of the conjugated π -plane, and $\mathbf{v} = \mathbf{w} \times \mathbf{u}$. Bonded interactions are derived systematically in a bottom-up manner from a Boltzmann inversion of the atomistic conformational distribution functions. The non-bonded interaction potential between two particles i and j is, by contrast, defined in a top-down way as

$$V_{\text{nb}}^{(ij)} = u(r_{ij}) \left[\kappa - \frac{2\nu}{3} A_i : A_j - \frac{2\mu}{3} (A_i : B_j + B_i : A_j) - \frac{\lambda}{2} B_i : B_j \right]. \quad (2.14)$$

Here, the volume overlap $u(r_{ij})$ of density clouds associated with each particle governs the interaction strength. The interaction parameter κ controls the compressibility of the system. Orientational interactions are defined in terms of the particle tensors

$$A_{i,\alpha\beta} = \frac{1}{2} (3u_\alpha u_\beta - 1), \quad (2.15)$$

$$B_{i,\alpha\beta} = v_\alpha v_\beta - w_\alpha w_\beta. \quad (2.16)$$

In the potential from Eq. 2.14, the interaction parameters ν and λ generate a nematic and biaxial alignment, respectively, whereas μ effects an orthogonal alignment between the interaction partners, not required (as unphysical) in this context. The phenomenological potential thus mimics the π - π interaction between conjugated subunits. Realistic values for ν and λ can be derived from the mechanical properties of the polymer, and are on the order of several $k_B T$ [26, 27]. By tuning their relative strengths, it is furthermore possible to simulate amorphous, nematic and biaxial systems within the same framework.

As a considerable advantage of the above approach, the orientation of the particles is known throughout the entire simulation. Backmapping of the atomistic structures without loss of orientational π - π ordering is hence possible. A work-

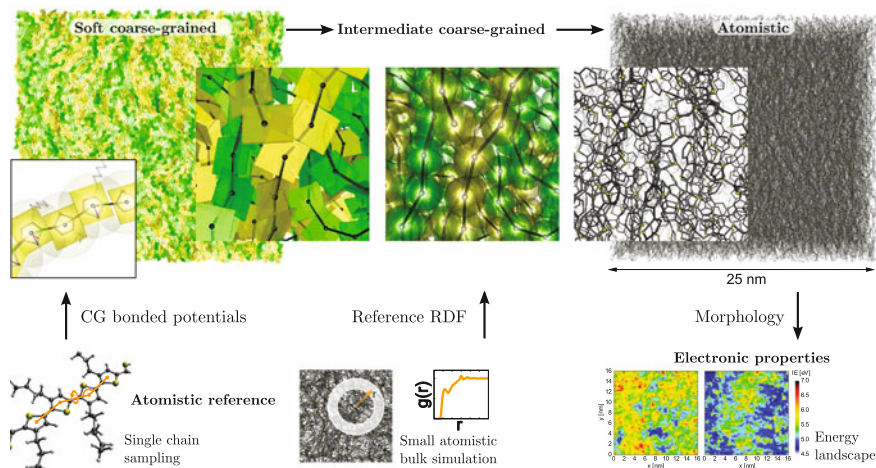


Fig. 2.7 Workflow for the simulation of large models of conjugated polymers at atomistic resolution [28]. A low-resolution polymeric mesophase is simulated with a soft coarse-grained description that incorporates phenomenological non-bonded interaction potentials and bonded interactions derived from coarse-graining of an atomistic chain. Backmapping of the low-resolution model proceeds via an intermediate coarse-grained step that removes chain overlaps inherited from the soft interaction potential. Finally, atomistic details are backmapped into the coarse-grained representation, with the resulting atomistic configuration relaxed via molecular dynamics

flow [28] for the simulation of polymeric mesophases then comprises the following steps (see Fig. 2.7): First, coarse-grained bonded potentials are derived from an atomistic reference simulation of a single chain, using Boltzmann inversion. Second, large polymeric mesophases of the respective polymer are prepared and equilibrated via Metropolis Monte-Carlo sampling with appropriately defined Monte-Carlo moves. Third, the excluded volume of the chains is recovered by applying an intermediate coarse-grained potential to the particles, derived from structure-based coarse-graining of an all-atom polymer melt. Fourth, the atomistic details are reinserted, and the obtained structure equilibrated via atomistic MD.

Well exceeding the capability of purely atomistic simulations, simulation protocols based on soft coarse-grained models enable us to study the effect of long-range conformational disorder on electronic properties, as will be exemplified in Chap. 5 for the polymeric semiconductor P3HT.

2.2.5 Lattice Models

In order to study structure-property relationships in organic semiconductors, we usually require a systematic link of the theoretical description to the underlying chemical structures. At an atomistic level of resolution, this requirement is of course

met, and still holds true for most coarse-grained treatments with potentials derived from an atomistic reference. Sometimes, however, more generic descriptions—here in the form of lattice models—are desirable: We will use them to distinguish between essential and non-essential features of a model, to explore finite-size effects, or to study complex morphologies (such as patterned thin films) where preassembly on an atomistic scale is artefact-prone. This broad range of applicability is due to the straightforward parametrization and efficient equilibration of such lattice models.

Within the lattice description, particles positioned at the lattice sites represent entire molecules, with their interactions defined in diverse ways to satisfy the purpose of the model. In the simplest case, the anisotropic sites are modelled as multipolar polarizable particles with fixed orientation—i.e., they are simply arrested in their initial, preassembled configuration. This type of lattice description will prove useful for the study of multi-layered and patterned thin films (Sect. 4.2).

Based on phenomenological Hamiltonians, disordered structures can be obtained efficiently through equilibration of the structures using Monte-Carlo techniques. To study the formation and energetics in polycrystalline systems (see Fig. 2.2c and Sect. 4.4), for example, several (approximately) periodically matched sublattices assembled from unit cells with varying orientations are superimposed and seeded independently. The individual grains then grow probabilistically around those seeds with only exclusion interactions applied: $V(i, j) = \infty$ if $r_{ij} \leq r_c$, else 0, with particle indices i, j and cutoff r_c .

Furthermore, Ising- and Heisenberg-type models can be used to address intrinsically disordered materials. The effects of interface roughness, for example, will be described based on a morphology simulated with a binary 3D Ising model (see Fig. 2.2b and Sect. 6.1.3), where the magnetization variable determines the chemical identity (donor D or acceptor A) of the lattice particle, with phenomenological contact interactions chosen such that $\varepsilon_{AD} = \varepsilon_{DA} < \varepsilon_{AA} = \varepsilon_{DD}$. The chemical composition of the system is furthermore constrained by only admitting particle swaps as Monte-Carlo moves.

Finally, Heisenberg-type models access disorder-dependent properties in multipolar bulk media, notably the spatial correlation function of the site-energy landscape for charge transport, as well as associated finite-size effects. With the option to be parametrized from microscopic input, an interaction potential similar to Eq. 2.14 with an additional electrostatic contribution ($Q_i^i T_{tu}^{ij} Q_u^j$ with interaction tensor T_{tu}^{ij} and spherical-tensor multipole components Q_i^i) serves as the model basis:

$$V_{\text{nb}}^{(ij)} = \sum_{t,u} Q_t^i T_{tu}^{ij} Q_u^j - u(r_{ij}) \left[\frac{2\nu}{3} A_i : A_j + \frac{\lambda}{2} B_i : B_j \right]. \quad (2.17)$$

Due to the positional constraints of the lattice sites, the compressibility has been omitted from the interaction potential. Different from the soft coarse-grained case, $u(r_{ij})$ is now a function which is constant for nearest neighbours and zero beyond. With electrostatics modelled separately, the interaction terms controlled by ν and λ should be interpreted as only steric contributions. Already for the case of purely

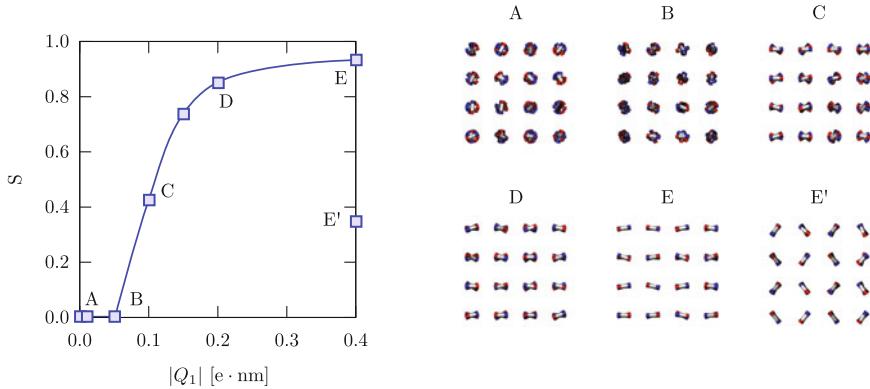


Fig. 2.8 Classical Heisenberg-type lattice model of a dipolar material. Phase behaviour of the nematic order parameter S with dipole strength $|Q_1|$ extracted from simulations of a cubic lattice with 125000 sites. In the excerpts from the snapshots (A–E’), each lattice site is represented as a small cylinder with the negative (positive) pole coloured blue (red). The ordering varies from amorphous (A,B) to dimerized (D,E). For comparison, the dipole strengths of the amorphous semiconductor Alq3 (resembling structure B) and crystalline donor-acceptor compound AAE007 (resembling structure D) amount to $|Q_1| = 0.1$ and $|Q_2| = 0.2$, respectively

dipolar interactions ($\nu = \lambda = 0$) as shown in Fig. 2.8, different types of ordering can be explored, ranging from amorphous to dimerized-crystalline.

2.3 Charge Transport Networks

The directed graph for charge (and similarly energy) transport derives from a site-based abstraction of the atomistic morphology obtained within one of the frameworks presented in Sect. 2.2. In the following, we will address the mapping procedure and in particular the parametrization of the network. As the latter has to be based on a specific transport theory, we will swiftly review the physics of charge transfer reactions in molecular systems.

2.3.1 Charge Transfer Reactions

For the bimolecular charge transfer reaction $A^\pm + B \rightarrow A + B^\pm$ between molecules A and B, a helpful model Hamiltonian reads [29–31]

$$\hat{H}_{AB} = U_{Ab}|\phi_{Ab}\rangle\langle\phi_{Ab}| + U_{aB}|\phi_{aB}\rangle\langle\phi_{aB}| + J_{AB}|\phi_{Ab}\rangle\langle\phi_{aB}| + J_{AB}^*|\phi_{aB}\rangle\langle\phi_{Ab}|. \quad (2.18)$$

In this Hamiltonian, $|\phi_{Ab}\rangle$ denotes the wave function of the system with molecule A in its charged (upper-case A), and molecule B in its neutral (lower-case b) state, and vice versa for $|\phi_{aB}\rangle$. $U_{Ab} = U_{Ab}(\mathbf{R})$ and $U_{aB} = U_{aB}(\mathbf{R})$ are the associated on-site energies, which depend on the nuclear configuration $\mathbf{R}$. J_{AB} is the coupling that mediates the transfer process.

The above Hamiltonian is still rather general in the sense that it can describe different regimes of charge transport, as determined by the relative time scales of the electronic and nuclear degrees of freedom: Namely, $t_J \sim 1/J_{AB}$ suggests a time scale for the migration of the wave function of the excess charge from A to B , whereas $t_\xi \sim 1/\hbar\omega_\xi$ quantifies the time scale for nuclear vibrations with frequency ω_ξ . If $t_J \ll t_\xi$, the charge is delocalized on the time scale of nuclear motion and hence experiences the effective potential-energy surface (PES)

$$U_\pm(\mathbf{R}) = \frac{1}{2} \left(U_{Ab}(\mathbf{R}) + U_{aB}(\mathbf{R}) \pm \sqrt{[U_{Ab}(\mathbf{R}) + U_{aB}(\mathbf{R})]^2 + 4|J_{AB}|^2} \right), \quad (2.19)$$

obtained through diagonalization of the Hamiltonian from Eq. 2.18. In Fig. 2.9, this adiabatic PES is resolved along a promoting nuclear mode ξ , together with U_{Ab} and U_{bA} . The splitting of U_+ and U_- at the crossing point ξ^* amounts to $2|J_{AB}|$, and hence increases as the interaction between molecules A and B becomes stronger. In organic semiconductors, however, the intermolecular coupling J_{AB} remains small compared to intramolecular bond vibration energies due to the weak interaction between the molecules. As a result, $t_J \gg t_\xi$, suggesting a picture where the charge “hops” from one localized state to the other, while subjected to fast vibrational motion. These localized, *diabatic* states differ qualitatively from adiabatic states in that their character does *not* depend on the nuclear coordinates: Specifically, $|\phi_{Ab}\rangle$ defines the situation where the charge is localized on A whatever the nuclear configuration may be. A rigorous definition for these states hence reads

$$\langle \phi_\nu | \nabla_R | \phi_\mu \rangle = 0, \quad (2.20)$$

where ∇_R denotes the gradient with respect to the nuclear coordinates. In practice, a construction of these diabatic states, to be addressed later, is challenging if approached rigorously. We proceed by calculating the rate $k_{A \rightarrow B}$ for charge hopping between the diabatic states: As the intermolecular interaction that mediates J_{AB} is weak, this rate can be approximated using 1st-order perturbation theory. Fermi’s Golden Rule yields

$$k_{A \rightarrow B} = \frac{2\pi}{\hbar} \int f(\xi) |J_{AB}|^2 \delta(U_{Ab}(\xi) - U_{aB}(\xi)) d\xi, \quad (2.21)$$

where the integral accounts for a canonical average over all configurations ξ with the Boltzmann distribution function $f(\xi) \sim \exp[-U_{Ab}(\xi)/k_B T]$. Energy conservation, however, requires the transfer event to occur at the crossing point ξ^* , where $U_{Ab}(\xi) = U_{aB}(\xi)$. If the promoting mode is treated classically, we obtain the Marcus rate

expression [32]

$$k_{A \rightarrow B} = \frac{2\pi}{\hbar} \frac{|J_{AB}|^2}{\sqrt{4\pi\lambda k_B T}} \exp \left[-\frac{(\Delta U_{AB} - \lambda)^2}{4\lambda k_B T} \right]. \quad (2.22)$$

Here, λ denotes the classical reorganization energy that relates to the distortion of the molecular structure required to trigger the charge transfer:

$$\lambda = \frac{1}{2} \omega_\xi^2 (\xi_{Ab} - \xi_{aB})^2. \quad (2.23)$$

In principle, this reorganization energy also features electronic and nuclear polarization contributions from the environment that can be accounted for via an additional harmonic mode ξ' , giving rise to the outer-sphere reorganization energy

$$\lambda^{\text{out}} = \frac{1}{2} \omega_{\xi'}^{\text{out}^2} (\xi'_{Ab} - \xi'_{aB})^2. \quad (2.24)$$

The Marcus rate from Eq. 2.22 has been applied with considerable success to charge transfer in solution and in the solid state. The classical treatment of both the intra- and intermolecular vibrational modes used in its derivation is, however, only appropriate in the high-temperature regime, where $k_B T \gg \omega_\xi, \omega_{\xi'}$. At room temperature, these conditions are barely satisfied, considering that intramolecular bond vibrations have zero-point energies on the order of 0.1 eV. This exceeds the thermal energy at room temperature by a factor of four. A more rigorous approach therefore builds on a Hamiltonian which includes a quantum-mechanical description of both the electronic and nuclear degrees of freedom:

$$\hat{H}_{AB} = \sum_{k,l} (U_{Ab}^{kl} + U_{Ab}^{\text{out}}) |\psi_{Ab}^{kl}\rangle \langle \psi_{Ab}^{kl}| + \sum_{k,l} (U_{aB}^{kl} + U_{aB}^{\text{out}}) |\psi_{aB}^{kl}\rangle \langle \psi_{aB}^{kl}| + \quad (2.25)$$

$$\sum_{k,l,k',l'} J_{AB}^{klk'l'} |\psi_{Ab}^{kl}\rangle \langle \psi_{aB}^{k'l'}| + \text{h.c.} \quad (2.26)$$

Here, $|\psi_{Ab}^{kl}\rangle = |\phi_{Ab}\rangle |\chi_A^k\rangle |\chi_b^l\rangle$ is a product state with the nuclear wave functions χ_A^k and χ_b^l with vibrational quantum numbers k and l and frequency ω_A and ω_b , respectively. U_{Ab}^{out} and U_{aB}^{out} are the potentials that describe the coupling with a (still classical) outer-sphere mode. Assuming that the initial state from which the charge transfer reaction proceeds is the vibrational ground state with $k = l = 0$, we obtain for the charge transfer rate [4, 33]

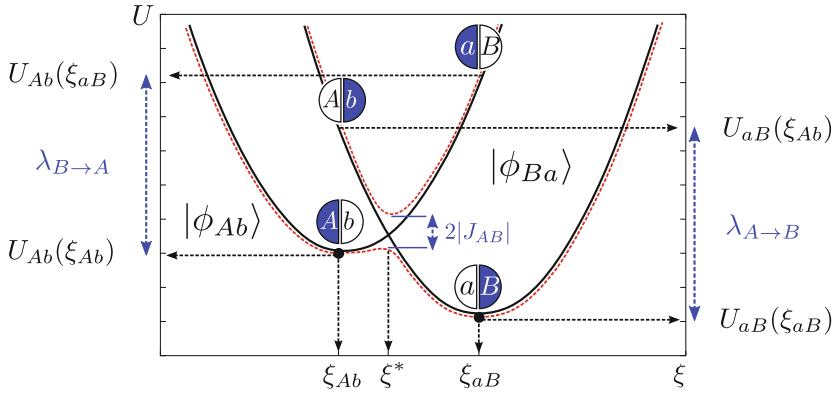


Fig. 2.9 Diabatic and adiabatic potential energy surfaces. Diabatic (solid black line) and adiabatic (dashed red line) potential energy surfaces of two electronic dimer states $|\phi_{Ab}\rangle$ and $|\phi_{Ba}\rangle$ participating in the charge transfer reaction along the reaction coordinate (promoting, accepting mode) ξ . The adiabatic level splitting at the crossing point ξ^* amounts to twice the electronic coupling J_{AB} . Furthermore shown are the reorganization energies $\lambda_{A \rightarrow B}$, $\lambda_{B \rightarrow A}$ (see Eq.2.33)

$$k_{A \rightarrow B} = \frac{2\pi}{\hbar} \frac{|J_{AB}|^2}{\sqrt{4\pi\lambda^{\text{out}}k_B T}} \sum_{k,l} |\langle \chi_A^0 | \chi_a^k \rangle|^2 |\langle \chi_b^0 | \chi_B^l \rangle|^2. \quad (2.27)$$

$$\cdot \exp \left[-\frac{(\Delta U_{AB} - \hbar k \omega_A - \hbar l \omega_B - \lambda^{\text{out}})^2}{4\lambda^{\text{out}}k_B T} \right]. \quad (2.28)$$

This expression, which ultimately simplifies to the Levich-Jortner [29, 34] rate expression, demonstrates explicitly how the charge transfer between the initial and final states is mediated by the nuclear degrees of freedom. This extended theory incorporates nuclear tunnelling important at low temperatures, where the charge transfer proceeds via tunnelling through the energy barrier in the PES [35]. Still, at very low temperatures, the description of charge transfer requires a yet more realistic account of the spectral density of the phonon bath, leading to rate expressions such as those developed by Weiss and Dorsey [36, 37].

2.3.2 Graph Generation and Parametrization

We have rationalized in the previous section that charge transfer in molecular materials proceeds as a hopping process between diabatic, localized states. Different rate expressions that describe this process based on a classical or quantum-mechanical account of the internal and/or external promoting mode all share two cardinal parameters, the electronic coupling J and driving force ΔU . The treatment of the internal and outer-sphere reorganization differs among the theories. In the Marcus picture,

however, nuclear reorganization can be captured within a single parameter λ . Among these three parameters that hence quantify the charge transfer process, J and ΔU strongly depend on the conformational and packing properties of the molecular dimer and, in the case of ΔU , also the molecular environment. To describe charge transport, these microscopic parameters have to be evaluated for all charge transfer pairs in an atomistically resolved morphology. These pairs and associated localization sites define the nodes and links, respectively, of a directed graph based on which charge transport in the system can be simulated.

System Partitioning

As a first step in generating the charge transport network, we have to partition the atomistic morphology onto localization sites or *conjugated segments*, which should be defined such that they correspond to the diabatic states in the Hamiltonian from Eq. 2.18. In small-molecular organic semiconductors, these conjugated segments correspond to entire molecules, within which charge delocalization is instantaneous. In polymeric systems, this simple assignment of localization sites may fail, as torsional defects along the conjugated backbone, variations in molecular fields, or electron-phonon interactions can enforce a stronger localization of the charge on a conjugated subunit, rather than delocalization along the entire polymer chain. In this case, one in principle has to calculate the wave function of the entire (sub-)system and thus identify the conjugated segments [38, 39]. The latter can be achieved via linear scaling methods such as the tight-binding approximation of DFT (DFTB) [40, 41]. A computationally less demanding, but crude [42] approach is to employ a heuristic criterion for conjugation [25, 26]: Polymer chains are then partitioned onto their units of transport based on a cutoff criterion for the torsional deviation from the planar *cis*- and *trans*-conformations of two successive repeat units.

Once the conjugated segments have been identified, they are further divided into *rigid fragments*, i.e., structural elements that are insensitive to the influence of thermal fluctuations. As an example, conjugated units such as a thiophene or benzene ring remain planar even at elevated temperatures. From the definition of these rigid fragments, local frames—required for electrostatic parametrizations as well as orbital mapping—are obtained in a straightforward manner. Furthermore, by mapping DFT-optimized structures onto the rigid fragments, bond-length fluctuations that may introduce artefacts in the calculation of electronic couplings can be avoided.

The connectivity of the conjugated segments is described via a neighbourlist storing pairs of conjugated segments between which charge transfer may occur. This neighbourlist is constructed based on a cutoff criterion for the nearest distance of approach between any of the rigid fragments of the two sites. Finally, with the set of pairs defining the links of the directed graph, the parametrization of the network requires the evaluation of backward- and forward-rates for each of these links.

Electronic Couplings

The off-diagonal element $J_{AB} = \langle \phi_{Ab} | H_{AB} | \phi_{aB} \rangle$ in the Hamiltonian from Eq. 2.18 quantifies the electronic coupling between the diabatic states $|\phi_{Ab}\rangle$ and $|\phi_{aB}\rangle$, mediated by the dimer Hamiltonian H_{AB} . Even with the conjugated segments A and B identified, these diabatic states still need to be constructed. As a rigorous deriva-

tion via Eq. 2.20 is involved, approximate constructions, using techniques such as constrained DFT, are preferred [43, 44]. The cheapest solution, however, is to approximate the diabatic states via the single-site wave functions $|\phi_A\rangle$ and $|\phi_B\rangle$ of the two monomers that participate in the charge transfer. These wave functions are usually not orthogonal—a condition required for the $|\phi_{Ab}\rangle$ and $|\phi_{aB}\rangle$ in Eq. 2.18. The resulting off-diagonal elements in the overlap matrix

$$\tilde{S}_{AB} = \begin{pmatrix} 1 & S_{AB} \\ S_{AB} & 1 \end{pmatrix} \quad (2.29)$$

lead to artificial contributions to the couplings. To correct for these, a transformation of the secular equation $\tilde{H}_{AB}\mathbf{c} = \epsilon\tilde{S}_{AB}\mathbf{c}$ into a standard eigenvalue equation of the form $\tilde{H}_{AB}\mathbf{c} = \epsilon\mathbf{c}$ is required [45], where $\mathbf{c}$ denotes the vector of expansion coefficients. Starting from $\tilde{H}_{AB}$ in the approximate, diabatic basis,

$$\tilde{H}_{AB} = \begin{pmatrix} \bar{U}_{Ab} & \bar{J}_{AB} \\ \bar{J}_{AB} & \bar{U}_{aB} \end{pmatrix}. \quad (2.30)$$

the overlap-corrected electronic couplings to be used in the Marcus or Levich-Jortner rate expressions result after a transformation $\tilde{S}_{AB}^{-1/2}\tilde{H}_{AB}\tilde{S}_{AB}^{-1/2}$ as

$$J_{AB} = \frac{\bar{J}_{AB} - \frac{1}{2}(\bar{U}_{Ab} + \bar{U}_{aB})S_{AB}}{1 - S_{AB}^2}. \quad (2.31)$$

To obtain J_{AB} , it is therefore sufficient to calculate $\bar{J}_{AB} = \langle\phi_A|H_{AB}|\phi_B\rangle$ using the non-orthogonal, approximate diabatic states. The Dimer-Projection (DIPRO) method [45] implemented in VOTCA computes these couplings efficiently based on the frozen-core approximation (thus assuming that only the HOMO and LUMO orbitals participate in the hole- or electron-transfer, respectively) through projection of the monomer states onto the dimer states $\{\phi_{AB}^i\}$:

$$\bar{J}_{AB} = \sum_{i,j} \langle\phi_A|\phi_{AB}^i\rangle \langle\phi_{AB}^i|H_{AB}|\phi_{AB}^j\rangle \langle\phi_{AB}^j|\phi_B\rangle. \quad (2.32)$$

We note, however, that the DIPRO formalism still requires three DFT calculations per pair, two monomer and one dimer calculation. For large systems with on the order of 10^4 pairs, this implies a considerable computational expense. Though compromising on accuracy, a semi-empirical ZINDO-based approach [46, 47] parametrized for molecules with light atomic elements up to Cl can then be the preferred option. This approach (implemented in VOTCA::MOO) reduces the computational cost to a single monomer calculation per molecule *type* by constructing the diabatic states of a specific pair through appropriate rotations of the atomic orbitals onto the predefined rigid fragments.

Reorganization Energies

In a classical treatment of the intramolecular vibrations as used in the Marcus picture, the molecular reorganization is absorbed into two reorganization energies for the charging and discharging process:

$$\begin{aligned}\lambda_{A \rightarrow B} &= U_a(\xi_A) - U_a(\xi_a) + U_B(\xi_b) - U_B(\xi_B), \\ \lambda_{B \rightarrow A} &= U_b(\xi_B) - U_b(\xi_b) + U_A(\xi_a) - U_A(\xi_A).\end{aligned}\quad (2.33)$$

The notation follows the convention from Sect. 2.3.1: U_a and U_A , for example, denote the PES of molecule A in its neutral and charged state, respectively, evaluated with the nuclear configuration (ξ) of either the neutral (ξ_a) or charged (ξ_A) state. The reorganization energies are hence approximated via four points on the PES of each molecule, requiring a total of four SCF calculations per molecule. If the reorganization energy is assumed to not strongly fluctuate among pairs, these calculations only have to be carried out once per molecule type. In doing so, one should additionally consider that the structural reorganization in the solid state is usually sterically constrained, in particular in π -stacked arrangements. In the gas-phase estimations of the reorganization energy, large conformational changes (notably ring rotations) should hence be prevented through appropriately chosen coordinate constraints.

Driving Forces

The site energy difference of the segments in the charge transfer pair determines the driving force $\Delta U_{AB} = U_A - U_B$ for the charge transfer reaction. For hole and electron transfer, these site energies are determined by the ionization energy and electron affinity, respectively. Due to electrostatic interactions with the molecular environment, they sensitively depend on the local and even global morphology of the material. However, as the intermolecular (as opposed to intramolecular) fields are weak, a perturbative treatment is adequate, leading to

$$\begin{aligned}U_A &= U_A(\xi_A) - U_a(\xi_a) = (U_A^{\text{int}}(\xi_A) - U_a^{\text{int}}(\xi_a)) + \\ &+ (W_A^{(1)} - W_a^{(1)}) + (W_A^{(2)} - W_a^{(2)}).\end{aligned}\quad (2.34)$$

For U_B , an analogous expression holds. The first-order correction ($W_A^{(1)} - W_a^{(1)}$) captures the electrostatic, the second-order correction ($W_A^{(2)} - W_a^{(2)}$) the polarization contribution to the gas-phase site energy $U_A(\xi_A) - U_a(\xi_a)$. Finally, if the charge transfer reaction occurs under the influence of an externally applied field $\mathbf{E}$, an additional field term $-q\mathbf{E}(\mathbf{r}_A - \mathbf{r}_B)$ has to be added to the site-energy difference.

Site-energy calculations are associated with a substantial computational expense, since the perturbative corrections in Eq. 2.34 have to be evaluated for each segment in the system. We will describe in detail in Chap. 3 how this can be achieved within a MM/MM or QM/MM long-range polarized embedding approach.

2.4 Charge-Carrier Dynamics and Mobility

With the transport graph fully parametrized, charge-carrier dynamics are described by a Master equation of the form

$$\partial_t P_I(t) = \sum_J [P_J(t) K_{J \rightarrow I} - P_I(t) K_{I \rightarrow J}], \quad (2.35)$$

with transition rates $K_{I \rightarrow J}$, $K_{J \rightarrow I}$ and time-dependent state occupation probabilities $P_I(t)$, $P_J(t)$. In the special case of a single charge carrier ($N = 1$) drift-diffusing through the system, there is a one-to-one correspondence between states and localization sites. The general expression from Eq. 2.35 then simplifies to

$$\partial_t p_A(t) = \sum_B [p_B(t) k_{B \rightarrow A} - p_A(t) k_{A \rightarrow B}], \quad (2.36)$$

with the *site* (rather than state) occupation probabilities $p_A(t)$, $p_B(t)$ and charge transfer rates $k_{A \rightarrow B}$, $k_{B \rightarrow A}$ between the conjugated segments A and B . For $N > 1$, i.e., multiple charge carriers, the number of system configurations increases dramatically. For system sizes on the order of $M = 10^3 - 10^5$ sites, direct solution of the dynamical equations is in this case prohibitive, due to the large manifold of states ($\sim M^N$) as well as non-linearities that result from the interaction between the charge carriers. Kinetic Monte-Carlo (KMC) techniques [48, 49] are then the method of choice: Here, the carrier trajectories are simulated explicitly as a Markov process, with the time coordinate propagated according to the Variable-Step-Size Method (VSSM). The latter is mandatory as charge transfer rates may span many orders of magnitude, leading to site escape times anywhere from 10^{-15} to 10^{-9} s.

In the KMC approach, charge transfer rates can be updated on the fly to take, for example, the Coulomb interaction between charge carriers into account. Furthermore, the formalism easily accommodates multiple types of electronic states (excitons, charges and charge-transfer states) including their interactions and mutual conversions—provided, of course, the transport graph has been parametrized accordingly.

Within the kinetic description, physical observables result as averages over the explicit trajectories. One such observable is the charge-carrier mobility tensor $\tilde{\mu}$, which can be calculated directly from the site occupation fractions:

$$\tilde{\mu}_{\alpha\beta} = \frac{1}{N|\mathbf{F}|^2} \sum_{A,B} k_{A \rightarrow B} p_A (1 - p_B) (R_{A,\alpha} - R_{B,\alpha}) F_\beta. \quad (2.37)$$

Here, the exclusion term $(1 - p_B)$ reflects the constraint that sites must only be singly occupied. Alternatively, the mobility is obtained as an end-point average over individual trajectories with net displacement ΔR after time T ,

$$\tilde{\mu}_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^N \frac{\Delta R_{\alpha} F_{\beta}}{T|\mathbf{F}|^2}. \quad (2.38)$$

The macroscopic charge-carrier mobility is thus computed as a function of temperature, charge-carrier density and field strength, where, however, finite-size effects inherent to microscopic simulations may have to be accounted for, especially at low temperatures, small charge-carrier densities, and/or large energetic disorder [50, 51]. The results from such simulations can finally be used to parametrize continuous drift-diffusion models [52], and in this way calculate I-V curves of simple electronic devices.

References

1. A. Troisi, D.L. Cheung, D. Andrienko, Charge transport in semiconductors with multiscale conformational dynamics. *Phys. Rev. Lett.* **102**(11), 116602 (2009)
2. T. Vehoff, Y.S. Chung, K. Johnston, A. Troisi, D.Y. Yoon, D. Andrienko, Charge transport in self-assembled semiconducting organic layers: role of dynamic and static disorder. *J. Phys. Chem. C* **114**(23), 10592–10597 (2010)
3. D.P. McMahon, A. Troisi, Organic semiconductors: impact of disorder at different timescales. *Chem. Phys. Chem.* **11**(10), 2067–2074 (2010)
4. V. Rühle, A. Lukyanov, F. May, M. Schrader, T. Vehoff, J. Kirkpatrick, B. Baumeier, D. Andrienko, Microscopic simulations of charge transport in disordered organic semiconductors. *J. Chem. Theory Comput.* **7**(10), 3335–3345 (2011)
5. R.M. Martin, *Electronic Structure: Basic Theory and Practical Methods* (Cambridge University Press, New York, 2004). ISBN 0521782856
6. A. Szabo, N.S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure theory* (Dover Publications, New York, 1996). ISBN 0486691861
7. R. Ditchfield, Self-consistent molecular-orbital methods. IX. an extended gaussian-type basis for molecular-orbital studies of organic molecules. *J. Chem. Phys.* **54**(2), 724 (1971)
8. D. Frenkel, *Understanding Molecular Simulation: From Algorithms to Applications*. Computational Science Series, 2nd edn. (Academic Press, San Diego, 2002). ISBN 0122673514
9. H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, A. DiNola, J.R. Haak, Molecular dynamics with coupling to an external bath. *J. Chem. Phys.* **81**(8), 3684 (1984)
10. G. Bussi, D. Donadio, M. Parrinello, Canonical sampling through velocity rescaling. *J. Chem. Phys.* **126**(1), 014101 (2007)
11. H.J.C. Berendsen, D. van der Spoel, R. van Drunen, GROMACS: a message-passing parallel molecular dynamics implementation. *Comput. Phys. Commun.* **91**(1–3), 43–56 (1995)
12. W.L. Jorgensen, J. Tirado-Rives, The OPLS [optimized potentials for liquid simulations] potential functions for proteins, energy minimizations for crystals of cyclic peptides and crambin. *J. Am. Chem. Soc.* **110**(6), 1657–1666 (1988)
13. D.J. Wales, J.P.K. Doye, Global optimization by basin-hopping and the lowest energy structures of Lennard-Jones clusters containing up to 110 atoms. *J. Phys. Chem. A* **101**(28), 5111–5116 (1997)
14. C. Poelking, D. Andrienko, Effect of polymorphism, regioregularity and paracrystallinity on charge Transport in Poly(3-hexylthiophene) [P3ht] nanofibers. *Macromolecules* **46**(22), 8941–8956 (2013)
15. C. Poelking, *Charge Transport Simulations in Polymeric Semiconductors*, MSc thesis, University of Heidelberg, 2013

16. D. Wynands, M. Erber, R. Rentenberger, M. Levichkova, K. Walzer, K.-J. Eichhorn, M. Stamm, Spectroscopic ellipsometry characterization of vacuum-deposited organic films for the application in organic solar cells. *Org. Electron.* **13**(5), 885–893 (2012)
17. K. Kremer, F. Müller-Plathe, Multiscale simulation in polymer science. *Mol. Simul.* **28**(8–9), 729–750 (2002)
18. A.P. Lyubartsev, A. Laaksonen, Calculation of effective interaction potentials from radial distribution functions: a reverse Monte Carlo approach. *Phys. Rev. E* **52**(4), 3730–3737 (1995)
19. S. Izvekov, G.A. Voth, A multiscale coarse-graining method for biomolecular systems. *J. Phys. Chem. B* **109**(7), 2469–2473 (2005)
20. M.S. Shell, The relative entropy is fundamental to multiscale and inverse thermodynamic problems. *J. Chem. Phys.* **129**(14), 144108 (2008)
21. D.M. Huang, R. Faller, K. Do, A.J. Moulé, Coarse-grained computer simulations of polymer/fullerene bulk heterojunctions for organic photovoltaic applications. *J. Chem. Theory Comput.* **6**(2), 526–537 (2010)
22. E. Jankowski, H.S. Marsh, A. Jayaraman, Computationally linking molecular features of conjugated polymers and fullerene derivatives to bulk heterojunction morphology. *Macromolecules* **46**(14), 5775–5785 (2013)
23. K.N. Schwarz, T.W. Kee, D.M. Huang, Coarse-grained simulations of the solution-phase self-assembly of poly(3-hexylthiophene) nanostructures. *Nanoscale* **5**(5), 2017 (2013)
24. A. Lukyanov, A. Malafeev, V. Ivanov, H.-L. Chen, K. Kremer, D. Andrienko, Solvated poly(phenylene vinylene) derivatives: conformational structure and aggregation behavior. *J. Mater. Chem.* **20**(46), 10475 (2010)
25. V. Rühle, J. Kirkpatrick, D. Andrienko, A multiscale description of charge transport in conjugated oligomers. *J. Chem. Phys.* **132**(13), 134103–134109 (2010)
26. P. Gemünden, C. Poelking, K. Kremer, D. Andrienko, K.C. Daoulas, Nematic ordering, conjugation, and density of states of soluble polymeric semiconductors. *Macromolecules* **46**(14), 5762–5774 (2013)
27. P. Gemünden, K.C. Daoulas, Fluctuation spectra in polymer nematics and Frank elastic constants: a coarse-grained modelling study. *Soft Matter* **11**(3), 532–544 (2015)
28. P. Gemünden, C. Poelking, K. Kremer, K. Daoulas, D. Andrienko, Effect of mesoscale ordering on the density of states of polymeric semiconductors. *Macromol. Rapid Commun.* **36**(11), 1047–1053 (2015)
29. V. May, O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems*, 3rd edn. (Wiley-VCH, 2011). revised and enlarged edition edition, ISBN 3527407324
30. J.-L. Brédas, D. Beljonne, V. Coropceanu, J. Cornil, Charge-transfer and energy-transfer processes in π -conjugated oligomers and polymers: a molecular picture. *Chem. Rev.* **104**(11), 4971–5004 (2004)
31. A. Troisi, Charge transport in high mobility molecular semiconductors: classical models and new theories. *Chem. Soc. Rev.* **40**(5), 2347 (2011)
32. R.A. Marcus, On the theory of oxidation-reduction reactions involving electron transfer. I. *J. Chem. Phys.* **24**(5), 966 (1956)
33. F. May, *Charge-Transport Simulations in Organic Semiconductors*. Ph.D. thesis, Johannes-Gutenberg-Universität Mainz, 2012
34. J. Jortner, Temperature-dependent activation energy for electron transfer between biological molecules. *J. Chem. Phys.* **64**(12), 4860 (1976)
35. K. Asadi, A.J. Kronemeijer, T. Cramer, L.J.A. Koster, P.W.M. Blom, D.M. de Leeuw, Polaron hopping mediated by nuclear tunnelling in semiconducting polymers at high carrier density. *Nat. Commun.* **4**, 1710 (2013)
36. H. Grabert, U. Weiss, Quantum tunneling rates for asymmetric double-well systems with ohmic dissipation. *Phys. Rev. Lett.* **54**(15), 1605–1608 (1985)
37. P.A.M. Fisher, A.T. Dorsey, Dissipative quantum tunneling in a biased double-well system at finite temperatures. *Phys. Rev. Lett.* **54**(15), 1609–1612 (1985)
38. N. Vukmirovic, L.-W. Wang, Density of states and wave function localization in disordered conjugated polymers: a large scale computational study. *J. Phys. Chem. B* **115**(8), 1792–1797 (2011)

39. T. Liu, A. Troisi, Understanding the microscopic origin of the very high charge mobility in PBTTT: tolerance of thermal disorder. *Adv. Funct. Mater.* **24**(7), 925–933 (2014)
40. D. Porezag, T. Frauenheim, T. Köhler, G. Seifert, R. Kaschner, Construction of tight-binding-like potentials on the basis of density-functional theory: application to carbon. *Phys. Rev. B* **51**(19), 12947–12957 (1995)
41. M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, T. Aernouts, S. Suhai, G. Seifert, Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties. *Phys. Rev. B* **58**(11), 7260–7268 (1998)
42. H. Ma, T. Qin, A. Troisi, Electronic excited states in amorphous MEH-PPV polymers from large-scale first principles calculations. *J. Chem. Theory Comput.* **10**(3), 1272–1282 (2014)
43. T. Van Voorhis, T. Kowalczyk, B. Kaduk, L.-P. Wang, C.-L. Cheng, W. Qin, The diabatic picture of electron transfer, reaction barriers, and molecular dynamics. *Annu. Rev. Phys. Chem.* **61**(1), 149–170 (2010)
44. W. Qin, T. Van Voorhis, Extracting electron transfer coupling elements from constrained density functional theory. *J. Chem. Phys.* **125**(16), 164105 (2006)
45. B. Baumeier, J. Kirkpatrick, D. Andrienko, Density-functional based determination of intermolecular charge transfer properties for large-scale morphologies. *Phys. Chem. Chem. Phys.* **12**(36), 11103 (2010)
46. J. Kirkpatrick, An approximate method for calculating transfer integrals based on the ZINDO Hamiltonian. *Int. J. Quantum Chem.* **108**(1), 51–56 (2008)
47. V. Coropceanu, J. Cornil, D.A. da Silva Filho, Y. Olivier, R. Silbey, J.L. Brédas, Charge transport in organic semiconductors. *Chem. Rev.* **107**(4), 926–952 (2007)
48. D.T. Gillespie, A general method for numerically simulating the stochastic time evolution of coupled chemical reactions. *J. Comput. Phys.* **22**(4), 403–434 (1976)
49. K.A. Fichthorn, W.H. Weinberg, Theoretical foundations of dynamical Monte Carlo simulations. *J. Chem. Phys.* **95**(2), 1090 (1991)
50. A. Lukyanov, D. Andrienko, Extracting nondispersive charge carrier mobilities of organic semiconductors from simulations of small systems. *Phys. Rev. B* **82**(19), 193202 (2010)
51. B. Baumeier, O. Stenzel, C. Poelking, D. Andrienko, V. Schmidt, Stochastic modeling of molecular charge transport networks. *Phys. Rev. B* **86**(18) (2012)
52. S. Stodtmann, R.M. Lee, C.K.F. Weiler, A. Badinski, Numerical simulation of organic semiconductor devices with high carrier densities. *J. Appl. Phys.* **112**(11), 114909 (2012)

The (Non-)Local Density of States of Electronic
Excitations in Organic Semiconductors

Poelking, C.R.

2018, XIV, 133 p. 42 illus. in color., Hardcover

ISBN: 978-3-319-69598-3