11 Integration of Modelling at Various Length and Time Scales

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Abstract. Materials modelling tools have become increasingly integrated in the R&D portfolio. The unique insights available through simulation of materials at a range of scales, from the quantum and molecular, via the mesoscale to the finite element level, can provide discontinuous scientific advances. These tools are well validated and produce reliable, quantitative information. A key demand of academic and industrial research is that these tools become ever more integrated: integrated at each length and time scale with experimental methods and knowledge as well as integrated across the spectrum of scales in order to capture the multiscale nature of organisation in many materials.

This paper will address recent efforts in this direction. The principal focus will be on the derivation of accurate input parameters for mesoscale simulation, and the subsequent use of finite element modeling to provide quantitative information regarding the properties of the simulated mesoscale morphologies.

In mesoscale modeling the familiar atomistic description of the molecules is coarse-grained, leading to beads of fluid (representing the collective degrees of freedom of many atoms). These beads interact through pair-potentials which, crucially if meaningful data are to be obtained, capture the underlying interactions of the constituent atoms. The use of atomistic modeling to derive such parameters will be discussed. The primary output of mesoscale modeling is phase morphologies with sizes up to the micron level. These morphologies are of interest, but little prediction of the material properties is available with the mesoscale tools. Finite element modeling can be used to predict physical and mechanical properties of arbitrary structures. Details of the link that has been established between Accelrys' MesoDyn [11.1] and MatSim's Palmyra-GridMorph [11.2] are given and highlighted with some recent validation work on polymer blends. These results suggest that the combination of simulations at multiple scales can unleash the power of modeling and yield important insights.

11.1 Introduction

There are many levels at which modeling can be useful, ranging from the highly detailed ab initio quantum mechanics, through classical molecular modeling to process engineering modeling. These computations significantly reduce wasted experiment, allow products and processes to be optimized and

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permit large numbers of candidate materials to be screened prior to production.

Accelrys offers quantum mechanics, molecular mechanics and mesoscale technologies. These methods cover many decades of both length and time scale (see Table 11.1), and can be applied to arbitrary materials: solids, liquids, interfaces, self-assembling fluids, gas phase molecules and liquid crystals, to name but a few. There are a number of factors, which need to be taken care of to ensure that these methods can be applied routinely and successfully. First and foremost of course are the validity and useability of each method on its own, followed by their interoperability in a common and efficient user environment. These points are taken care of in state-of-the-art packages like the Materials Studio®[1] software [11.3] distributed by Accelrys.

Table 11.1. Comparison of scales of modeling: quantum, classical atomistic simulation and mesoscale modeling

	Quantum	Atomistic	Mesoscale
Length	Angstroms	nm	100s of nm
Fundamental Unit	Electrons/nuclei	atoms	Beads representing many atoms
Time scale	fs	ns	ms
Dynamics	Too expensive	F=ma	Hydrodynamics

Of equal importance of course is the integration of the simulation methods with experiment. In modern materials research and development, one needs to be able to move almost seamlessly from experimental knowledge to simulation and back again, requiring multiple input-output relationships at a range of materials length and time scales. These can take the form of

- Materials QSAR: quantitative structure -activity (property) relationships for materials aim to correlate molecular simulation results with experimental measurements of (macroscale) properties.
- Parameterisation of simulations: accurate materials simulations based on input parameters gained from detailed simulation as well as experimental data.
- Multiscale simulations, based on establishing the appropriate communication between the methods.

In the following, we shall give further detail and examples for each of these cases.

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[1] Materials Studio is a registered trademark of Accelrys Inc.

11.2 Structure-Activity and Structure-Property Approaches

Quantitative structure activity and property relationships (QSAR/QSPR) have long been used with great success in the life sciences. Based on experimental 'training set' data, correlations can be established between a range of molecular descriptors and biological activity. These correlations may take the form of equations derived by methods such as the Genetic Function Approximation [11.4], or neural networks. QSAR methods have proved to be powerful tools for the design of molecular libraries, investigating similarity and diversity as well as predicting properties.

Not surprisingly, such tools have also been applied successfully in a variety of materials cases as well [11.5, 11.6]. These statistical methods allow experimental information to be mined for important correlations, which can lead to deeper understanding of a material and optimised products. The correlations can be used to help design better materials. These new materials can be screened using the simulation methods and so an effective feedback loop is created which efficiently leads to new materials.

However, the complexity and multiscale nature of many materials and their properties pose particular challenges in the application of QSAR methods, which need to be address in future Materials QSAR tools. Firstly, there are many different materials classes with potentially very different sets of descriptors relevant to them. There is little knowledge so far about which are the most important ones relating for example to the prediction of permeability properties of polymer materials. Secondly, the calculation of the descriptors may involve simulations using methods at various scales, some of which may be computationally expensive.

11.3 Atomistic and Mesoscale Simulations and Their Parameterisation

Quantum, atomistic and mesoscale simulations provide valuable insights into the detailed physico-chemical behaviour of molecules and materials, and there are many properties, which can be determined directly from each, including structure, energies, stability, activity, diversity, solubility, adhesion, adsorption, diffusion, mechanical constants, spectra, and morphology. Ab initio quantum methods have the advantage that they can in principle be used for any element in the periodic table without specific parameterisation. They have been extensively developed so that one is now able to handle systems of a few hundred atoms routinely. For larger systems, however, methods requiring parameterisation are inevitable. In the following, we focus on force field developments for atomistic simulations and parameter determination for mesoscale simulations.

11.3.1 Atomistic Simulation

Fully atomistic simulation (where each atom is uniquely identified) is the core technology of polymer modelling. The methods use molecular mechanics, dynamics and Monte Carlo algorithms to probe the conformational and configurational behaviour of arbitrary materials. Most material properties can be inferred from these techniques, although properties that are fundamentally electronic (polarizability, dielectric constant, rates of chemical reaction, etc) are not the domain of classical simulation. The accuracy of property prediction relies on the force field, that is the mathematical expression used to create the potential function of the interacting components. These force fields comprise terms for: bond stretching, bond bending, torsional twisting, out of plane bending and pair-combinations of these. A typical force-field expression is given in 11.1.

$$
\begin{aligned}
E_{\mathrm{POT}} = & \sum_b D_b \left[1 - e^{-\alpha(b-b_0)}\right] + \sum_\theta H_\theta (\theta - \theta_0)^2 \\
& + \sum_\phi H_\phi \left[1 + s\cos(n\phi)\right] + \sum_\chi H_\chi \, \chi^2 \\
& + \sum_b \sum_{b'} (b - b_0)(b' - b'_0) + \sum_\theta \sum_{\theta'} F_{\theta\theta'} (\theta - \theta_0)(\theta' - \theta'_0) \\
& \sum_b \sum_\theta F_{b\theta} (b - b_0)(\theta - \theta_0) + \sum_\chi \sum_{\chi'} F_{\chi\chi'} \, \chi\chi' \\
& + \sum_\phi F_{\phi\theta\theta'} \cos\phi (\theta - \theta_0)(\theta' - \theta'_0) \\
& + \sum \varepsilon \left[\left(\frac{r^*}{r}\right)^{12} - 2\left(\frac{r^*}{r}\right)^{6}\right] + \sum q_i q_j / \varepsilon r_{ij}
\end{aligned}
\tag{11.1}
$$

Most force-fields are comparable in their accuracy for the minimum energy structure of simple molecules since they are parameterised to reproduce known behaviour. The true test of a force field is prediction of density and cohesive properties (heat of vaporization, solubility parameter, etc). For these properties the determining factor is the accuracy of non-bonded dispersion and electrostatic interactions (the last two terms in 11.1).

Accelrys has developed its own force field called COMPASS [11.7, 11.8], which stands for 'Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies'. It is an ab initio force field because most parameters are initially derived based on data determined by ab initio quantum mechanics calculations. Following this step, parameters are optimized on the basis of experimental data for condensed phase properties. In particular, thermophysical data for molecular liquids and crystals are used to refine the nonbond parameters via molecular dynamics simulations. The result is a highly accurate force field, which gives unsurpassed prediction for density and cohesive properties of a wide range of organic and some inorganic materials. The COMPASS force field is therefore a prime example of how accurate simulation at one scale (in this case electronic) and experimental data can be combined to great advantage in parameterisation of models at the next coarser scale (in this case atomistic).

As an example of the typical $< 1\%$ accuracy in density prediction which can be achieved with this method, Fig. 11.1 shows the comparison between experimental and predicted densities for perfluorobutane over a range of temperatures [11.9].

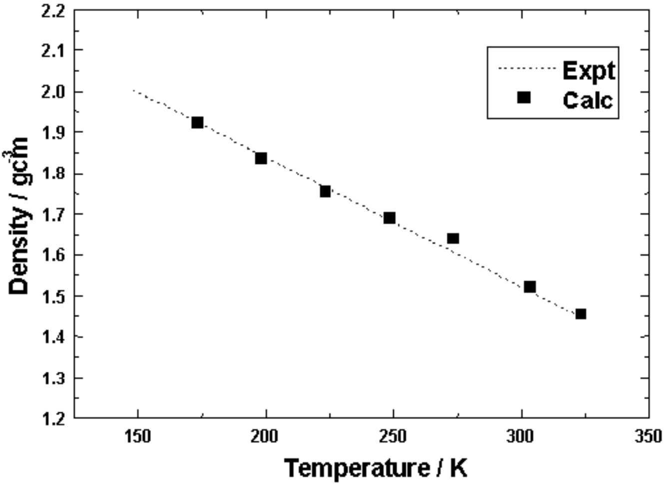


Fig. 11.1. Density versus temperature of perfluorobutane, comparing a fit to experimental data with values calculated from Molecular Dynamics simulations [11.9].

In Fig. 11.2 we show how COMPASS performs for the solubility parameter, which is the square root of the cohesive energy density [11.10]. It is crucial to be accurate in this parameter, in particular if mixture or diffusivity data is to be well reproduced. The toluene example shown in Fig. 11.2 [11.9] is just one of many validations, which show that Molecular Dynamics simulations with the COMPASS force field meet this demand. We can conclude that COMPASS gives highly accurate data for key properties of bulk materials.

11.3.2 Mesoscale Methods

In classical atomistic modelling, traditional Molecular Dynamics is used to obtain thermodynamic information about a pure or mixed system. Properties obtained using these microscopic simulations assume that the system is homogeneous in composition, structure and density, which is a limitation. When a system is complex, comprising several components, only sparingly miscible,

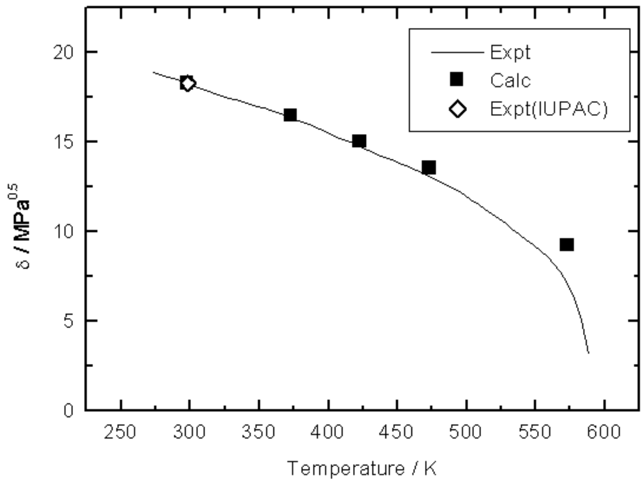


Fig. 11.2. The solubility parameter δ of toluene as a function of temperature. Calculations from molecular dynamics simulations with the COMPASS forcefield [11.9] agree well with a fit through experimental data and the official IUPAC value.

or the chain architecture is such that bulk phase separation is hampered by chemical bonds, exotic phases with remarkable properties can be observed. These so-called 'mesophases' comprise too many atoms for atomistic modeling to realistically describe. Hence coarse-grained methods (see Table 11.1) are better suited to such structures.

The primary techniques for mesoscale modeling are MesoDyn [11.11] and DPD [11.12]. These tools achieve longer length scales by uniting many atoms into a single bead, and longer time scales by integrating out the fast motions of the underlying particles leaving only soft, effective interactions. Complex self-assembling fluids, which have long-range order can be studied with these methods.

- MesoDyn
  MesoDyn is a dynamic mean-field density functional theory for complex fluids [11.13]. The free energy comprises an ideal term based on a Gaussian Chain Hamiltonian representation of the polymeric materials, a Gibbs entropy contribution favoring mixing and a non-ideal term accounted for using a mean-field approximation. The key approximation is that in the time regime under consideration the distribution functions are optimized (i.e. the free energy is minimal). Applying appropriate constraints the optimal distribution can be obtained and related back to the free energy. We are left with a simple expression for the non-ideal term (obtained by invoking the random phase approximation-RPA):

$$F^{\mathrm{nid}}_{\mathrm{RPA}}[\rho] = \frac{1}{2} \sum_{IJ} \int_V \varepsilon_{IJ}\, \rho_I(r) \rho_J(r)\, dr \tag{11.2}$$

Which assumes a local mean-field. However, the mean-field must account for the interchain interactions a non-local mean-field is preferred. A suitable choice leads to:

$$F^{\mathrm{nid}}[\rho] = \frac{1}{2} \int_V \int_V \varepsilon_{IJ} \left(|r - r'|\right) \rho_I(r) \rho_J(r')\, dr\, dr' \tag{11.3}$$

where $\varepsilon_{IJ}\left(|r - r'|\right)$ is a cohesive interaction defined by the same Gaussian kernel as in the ideal chain Hamiltonian. This parameter is then directly related to a calculable property, namely the Flory-Huggins interaction parameter χ.

- DPD
  DPD is a particle based method that uses soft-spheres to represent groups of atoms, and incorporates hydrodynamic behavior via a random noise, which is coupled to a pair-wise dissipation. These terms are coupled so as to obey the fluctuation-dissipation theorem. Groot and Warren [11.12] established the connection between a DPD fluid and a real fluid again relating the bead-bead interaction potential to the Flory-Huggins parameter χ. For a full description of DPD and some of its applications see [11.14] and [11.15].

The two methods overlap, but DPD is preferred where concentrations are low, and MesoDyn is ideal for systems, which comprise polymer melts and blends.

11.3.3 Applications of Mesoscale Modeling

The mesoscale techniques have been used to rationalize complex behaviour of latex emulsions for the paints, coatings and lubricants industries [11.16]. A series of simulations was undertaken to establish the link between latex-particle size distribution and the hydrophilic chain length of the non-ionic surfactants used to stabilize the emulsion. The more uniform the size distribution the more reliable the paint appearance and application rheology. Several MesoDyn calculations were performed with various chain lengths and a system, which led to optimal distribution of the latex particles was found. This was then taken to the laboratory where an improved formulation was established.

In the area of drug delivery DPD and MesoDyn have found many applications including formulation stability, active release profiles, compatibilization, effect of hydrophobic drugs on micelle sizes in a pluronic solution and the role of excipients. These complex problems are difficult to conceptualize, are poorly served by static theories and are critical to the efficacy of a novel drug formulation.

The effect of temperature on self-assembled structures of amphiphilic block copolymers in aqueous solution has been recently studied with MesoDyn [11.17]. While, according to Flory-Huggins theory, the interaction parameter has a simple inverse dependence on temperature ($\chi \sim 1/T$), it is well known that corrections need to be applied for most polymer blends and solutions. A more appropriate relationship for polymer solutions is the following

$$\chi = \alpha + \frac{\beta}{T} \tag{11.4}$$

In simple term, α represents a non-combinatorial entropic contribution, and β represents the enthalpic contribution. This expression was fitted to experimental data of interaction parameters between poly (ethylene oxide) and water, as well as poly (propylene oxide) and water, respectively. Typically, these data are determined experimentally by vapour pressure measurements. The resulting $\chi(T)$ could then be used in MesoDyn simulations of Pluronic P85 (triblock copolymer of ethylene oxide, propylene oxide, ethylene oxide, with certain chain lengths) in water for a range of temperatures.

The experimental phase diagram [11.18] shows the striking range of phases exhibited by such a relatively simple system. In particular, it shows that at polymer concentrations above about 20%, a micellar phase is observed at low temperatures, and rods or cylinders are formed above about $60°C$.

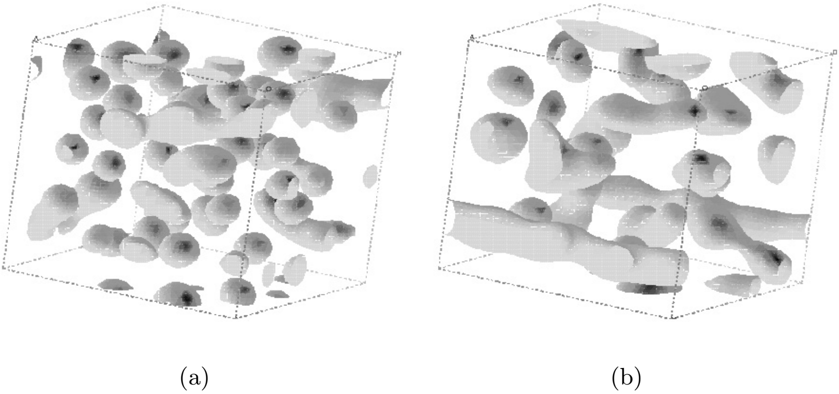
MesoDyn simulations were performed at these temperatures, and the resulting morphologies are show in Fig. 11.3(a) and 11.3(b). They are extremely encouraging, with definite evidence of the correct phase evolving at the correct temperature and composition.

11.4 Multiscale Modeling

11.4.1 From the Molecular to the Mesoscale

In order to integrate the molecular level and the mesoscale, the atomistic simulation results can be used to parameterise mesoscale simulation by providing sensible coarse-graining methods and effective interactions between species [11.17, 11.19].

One such example is the work by Vergelati and Spyriouni [11.19]. Their aim was to investigate the compatibility of a polyamide with a poly (vinyl acetate), where the acetate was systematically hydrolyzed towards the poly vinyl alcohol. The authors started on the atomistic level, using Discover Molecular Dynamics with the COMPASS force-field to determine cohesive energy densities of the various mixtures. The Flory-Huggins interaction parameters of the blends could then be calculated and used as input to MesoDyn simulations. The bead size parameters for MesoDyn were determined from the molecular weight and characteristic ratios of the polymers. Encouragingly, the length scale and morphology of the phase separation observed



(a) (b)

Fig. 11.3. (a) MesoDyn simulation of Pluronic PL85 in water at 27% concentration and temperature 15°C. The isodensity surfaces of the hydrophobic component are shown, clearly revealing the micellar structure. (b) Morphology after increase of temperature to 70°C, with the appropriate interaction parameter. The spherical micelles coalesce into rods, in line with experimental evidence.

in the simulation was found to match well with TEM results for the real materials.

A clear pathway has therefore been defined and is being more and more established for coarse-graining from the atomistic to the mesoscale. The major hole in the technology remains the reverse mapping from the mesoscale to the atomistic, where no adequate method has been developed.

11.4.2 From Mesoscale to Finite Element Simulation

The structures formed on the nanometer scale give rise to diverse and interesting material properties. As we have seen in the last section, mesoscale methods can be used with confidence to predict such structures. While some properties can be predicted directly from the mesoscale, property prediction given the knowledge of material structure and the property of the pure components that comprise the mixture has been developed widely in Finite Element Methods. An example of such a method, designed to deal with finely textured materials is Palmyra-GridMorph from MatSim [11.2]. Using standard solvers the finite element code can then predict the property for the realistic structured material.

As a test case for this combination of mesoscale and finite element methods we studied the oxygen diffusion through a material designed to act as a gas separation membrane. A binary blend of polystyrene and polybutadiene was simulated with MesoDyn using parameters obtained from atomistic level modeling. These polymers tend to phase segregate and large domains form with little interface. Upon addition of a diblock copolymer of the species (styrene and butadiene), the blend is compatibilized and the interfacial tension is lowered. The resulting morphology is far more complex with much smaller domains, more interfacial zones and frustrated regions. Both of these structures were analyzed for oxygen diffusion using GridMorph [11.20]. The pure component oxygen permaebilities for polystyrene and polybutadiene were obtained using the QSPR method Synthia [11.6, 11.21]. The results are given in Table 11.2.

Table 11.2. Oxygen permeability of two types of blends. Structures were simulated with MesoDyn, and permeabilities calculated for those structures using GridMorph.

System	Oxygen permeability (Dow Units)
Without Compatibilizer	970
With Compatibilizer	1040

The compatibilized blend shows increased permeability of oxygen, which can be attributed to an increase in the number of channels that the oxygen can choose to diffuse through. This study therefore uses atomistically obtained interaction energies and diffusivities to parameterize mesoscale methods and inform finite element tools, in order that mesoscopically calculated structures be analyzed for diffusion rates of the true material. This is an exciting development that we intend to pursue further.

11.5 Conclusion

The power of integrating modeling across different scales and with experimental data has been demonstrated. Combining experimental and simulation data in QSAR/QSPR methods generates valuable correlations and hence knowledge. Combining high quality measurements of some basic quantities (such as densities) with high-level simulations provides a successful parameterisation route for atomistic force field. Classical atomistic simulations with such a force field can then accurately predict material properties over a wide range of temperature, pressure and composition space. Furthermore, these simulations can in turn be used to derive input parameters for mesoscale simulations, while as above, additional experimental data can be used to hone the parameters further. A novel approach is to take the simulated mesoscale morphology as input to finite element methods in order to predict a wide range of material properties based on the morphology obtained. This now gives the modeler a route from the atomistic description of the system to a trust-worthy estimate of the properties of a material, obtained from the underlying molecules in a quantifiable manner.

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