STATISTICAL THERMODYNAMICS-BASED SIMULATION METHODS FOR THE PREDICTION OF POLYMER PROPERTIES

Doros N. Theodorou

School of Chemical Engineering, Department of Materials Science and Engineering, National Technical University of Athens, Zografou Campus, 157 80 Athens, Greece

ABSTRACT

Molecular simulations can quantitatively relate thermodynamic properties and phase equilibria to atomic-level structure and therefore serve as a basis for "molecular engineering design" of materials. For polymeric materials, however, the broad spectra of length scales and relaxation times governing structure and molecular motion pose severe challenges for conventional simulation techniques. Many of these challenges have been met by designing simulation methods based on the principles of statistical thermodynamics, which can sample complex configuration spaces efficiently. Examples of such methods include connectivity-altering Monte Carlo simulations, which enable the reliable prediction of equation of state properties, molecular packing, and entanglements in polymer melts; particle deletion (inverse Widom) methods for the calculation of solubilities of large molecules in polymers; and Gibbs-Duhem integration methods, based on the imposition of an artificial potential, to capture polymer melting points. Many problems are still not completely resolved, however, such as (a) how to coarse-grain the molecular representation into one involving fewer degrees of freedom; (b) how to address systems which do not achieve equilibrium over ordinary time scales, such as glasses; (c) how to deal with crack propagation and fracture.

INTRODUCTION

Molecular simulations are gaining ground as tools for the prediction of properties of a wide variety of physicochemical, materials, and biomolecular systems [1]. In materials science simulations are starting to be used within high-throughput screening strategies to optimize atomic-level structure for best performance in specific applications. This is exemplified by recent work on the design of nanoporous materials for methane storage [2].

One challenge faced by molecular simulations of materials is that accurate potentials for interatomic interactions are often unavailable. A second, perhaps more important challenge, is that structure and molecular motion in most materials of engineering interest are governed by very broad spectra of length and time scales, which are impossible to address with a single simulation technique. In response to these challenges, multiscale strategies are being developed, which extend from electronic structure calculations to atomistic molecular mechanics, molecular dynamics (MD), and Monte Carlo (MC) simulations, to mesoscopic methods, to formulations based on the continuum engineering sciences [3].

The challenge of long time scales is painfully clear in the case of polymeric materials. The longest relaxation times of polymer melts encountered in processing operations are typically on the order of ms to s. It is these broad spectra of relaxation times that are responsible for the complex viscoelastic behavior exhibited by polymer melts. On the other hand, the longest times that have been simulated with MD using classical force fields for interatomic interactions on specialized computational equipment are on the order of ms [4], with hundreds of ns being more typical of Beowulf clusters in university laboratories. Clearly, there are still several orders of magnitude on the time scale to be bridged in order to connect atomic-level structure with macroscopic performance.

Fortunately, one can devise simulation methods that can sample rugged potential energy hypersurfaces very efficiently and equilibrate atomistic or coarse-grained polymer models many orders of magnitude faster than "brute force" MD. These methods are based directly on the principles of statistical and macroscopic thermodynamics and take advantage of some geometric characteristics of macromolecular systems.

In this paper we will briefly present some examples of efficient equilibration strategies for polymers and estimates of thermodynamic properties and phase equilibria that are obtained from their application, mainly at the atomistic level. We will then outline remaining challenges to the development of reliable multiscale simulation strategies for polymers.

## EFFICIENT EQUILIBRATION STRATEGIES FOR POLYMERS

Connectivity-altering MC

MC algorithms that employ moves which rearrange the connectivity among polymer segments can dramatically enhance the equilibration of long-range conformational characteristics, such as the end-to-end distance and the radius of gyration. While the longest relaxation time of a real, or MD-simulated, long-chain melt scales with molar mass as $M^{3.4}$, the CPU time required by End-Bridging MC for the displacement of chain centers of mass to reach the root mean square end-to-end distance of chains, $\langle R^2 \rangle^{1/2}$, scales as M^{-1} [5]. Thus, the equilibration of long-chain polymer systems, well within the entangled regime, comes within reach. Predictions for the density as a function of M, for X-ray diffraction patterns and SANS single-chain structure factors are in excellent agreement with experiment, using force fields validated for small-molecule analogues [5] (see Figure 1).

Moreover, topological analysis of well-equilibrated long-chain configurations leads to estimates of the molar mass between entanglements, M_e, which are validated by plateau modulus measurements [6]. Recently, connectivity-altering MC has been used to elucidate how the melt density, entanglement properties, and cohesive energy density depend on short-chain branching in polyethylenes [7].
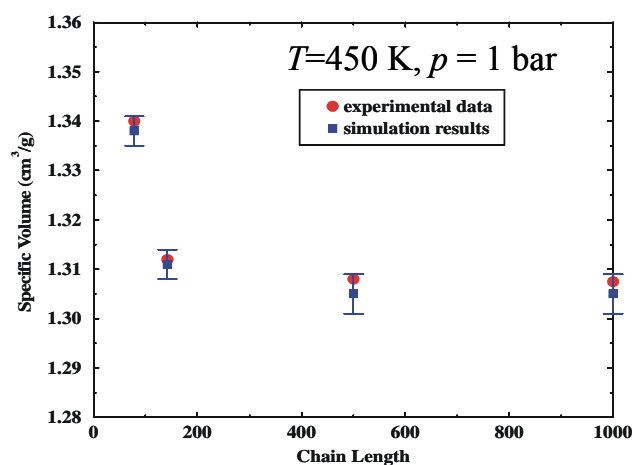
(a)
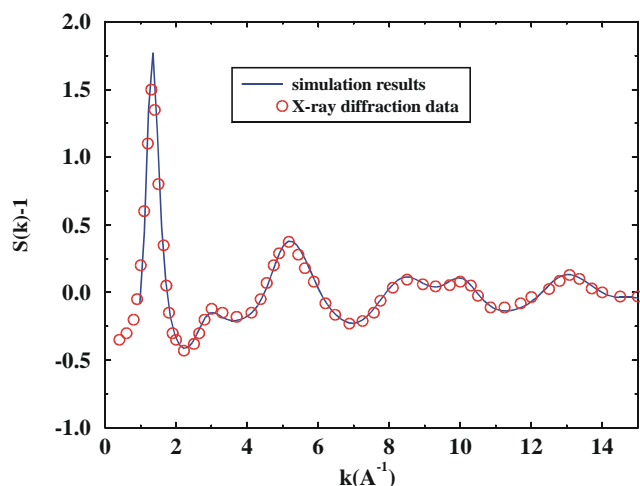
(b)

Figure 1: *(a) Specific volume as a function of chain length, in carbon atoms, for linear polyethylene melts at 450 K and 1 atm, as predicted by connectivity-altering Monte Carlo simulations and as measured experimentally; (b) Static structure factor as predicted from the simulations and as measured by X-ray diffraction.*

Particle Deletion for Chemical Potentials

The calculation of chemical potentials is central to the prediction of phase equilibria. Widom's test particle insertion [8] is an ingenious method for computing chemical potentials from simulation. Unfortunately, when the size of inserted molecules is large in comparison to clusters of accessible volume present in the matrix material, overlaps occur with overwhelming probability and a reliable estimation of the chemical potential becomes impossible.

A number of methods have been proposed to alleviate the insertion problem. One that has worked well for polymers is the particle deletion, or inverse Widom, method [9]. Here one estimates the chemical potential not by inserting a molecule, but rather by deleting an already existing molecule from the system. One has to realize that deleting a molecule does not lead to a typical configuration of the remaining system, but rather to a configuration that contains a hole. The bias associated with the hole can be rigorously removed through computationally efficient analytical calculations of the accessible volume. Application of the particle deletion method has led to excellent estimates of the solubility of large solvent molecules, such as benzene, in equilibrated polyethylene melts [10] (see Figure 2). Using the same method, it has been possible to capture sorption equilibria of compressed CO_2 in glassy atactic polystyrene, as well as swelling and plasticization effects caused by the sorption [11].
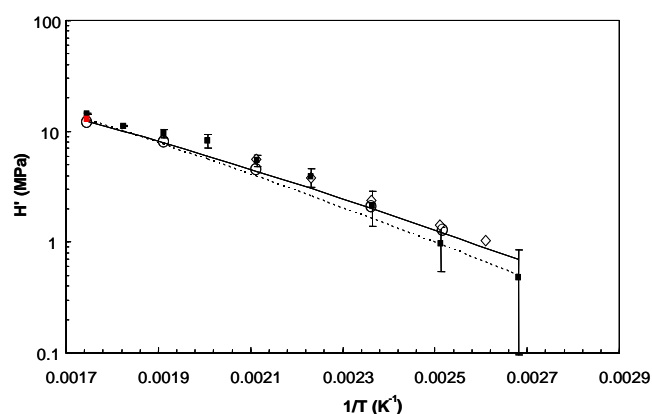

Figure 2: *Solubility of benzene in molten polyethylene as a function of temperature, as predicted by isothermal-isobaric MC simulations with the direct particle deletion method (filled points) [10] and as measured experimentally (open points). The solid and broken lines display estimates from the PC SAFT and the Lattice Fluid equations of state, respectively. The red point is a simulation estimate obtained from a simulation box of octuple volume, in order to establish that there are no system size effects. The solubility is expressed in terms of a weight fraction-based Henry's law constant, H'. H' is the ratio of the fugacity of benzene to the weight fraction of benzene in the polyethylene, in the limit where the latter weight fraction goes to zero.*

Melting Points Through Gibbs-Duhem Integration

Predicting the complex morphology and properties of semicrystalline polymers is a grand challenge for molecular simulation. Even the prediction of T_m, the equilibrium melting point of a polymer crystal, presents difficulties. By analogy to what is done for small-molecule materials, one can build a composite (sandwich) structure consisting of alternating crystalline and melt domains and try to determine T_m by MD as that temperature where none of the two types of domains increases at the expense of the other. Unfortunately, however, polymer crystal growth rates are too low to be observed reliably with MD. For example, the crystal growth

rate for high molar mass isotactic polypropylene (iPP) has been reported as 2.2 x 10⁻⁷ m s⁻¹. This means that, in order to observe growth of a facet by an average distance of 1 Å, one would need to simulate for 450 μs, a prohibitively long time.

One way to get around this problem is to introduce an artificial potential along polymer chains which encourages the adoption of helical conformations. The resulting system of stiffened chains has a much higher T_m which can be predicted reliably by MD, as the molecular dynamics there is fast. The objective then is to compute how the predicted T_m will change upon removal of the artificial potential. Starting from the condition of equality of chemical potentials between solid and liquid phases, one can derive, through straightforward thermodynamics, an expression for the derivative of T_m with respect to a parameter, λ, controlling the stiffness of the artificial potential. This expression involves only ensemble averaged energies and volumes of the individual solid and liquid phases at given λ, which can be extracted from single-phase simulations at fixed λ. Gibbs-Duhem integration of the derivative down to $\lambda=0$ gives T_m for the "real", unconstrained polymer [12]. Application of this strategy has yielded very good estimates of T_m for oligomers of iPP of various molar masses (Figure 3).
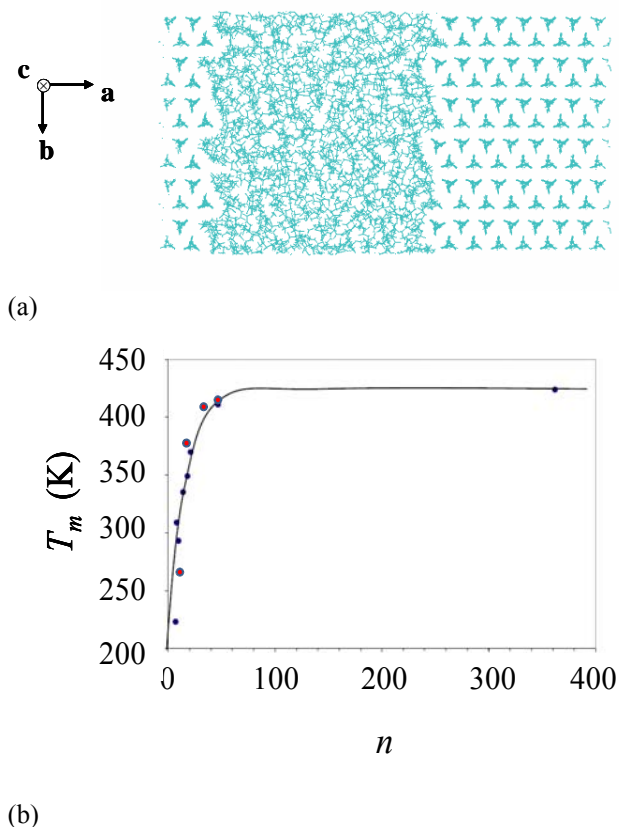

(a)

(b)

Figure 3: (a) "Sandwich" configuration of molten and crystalline isotactic polypropylene considered for the calculation of the melting point T_m. **a**, **b**, and **c** are the crystallographic axes of the monoclinic α1 form of isotactic polypropylene. At equilibrium, none of the two coexisting phases will grow against the other. (b) Equilibrium melting point of isotactic polypropylene at 1 atm as a function of chain length (number of repeat units n) , as predicted by MD simulations of the melt and crystal phases through a Gibbs-Duhem integration scheme (red points) [12] and as measured experimentally (blue points and line).

POLYMERS UNDER STRESS: CAVITATION OF RUBBERS

Statistical thermodynamics-based simulation methods are often called to provide insight into the stress-strain and terminal mechanical behaviour of polymeric materials. We briefly outline here a recently developed approach for exploring cavitation in rubbery polymers [13].

Cavitation, i.e. the development of cavities in a rubbery polymer subjected to hydrostatic tension, is a very important problem. The development of cavities in the rubbery primary coating between the inner core and the hard secondary coating of an optical fibre upon temperature cycling, due to thermal expansion mismatch, compromises light transmission through the fibre. Cavitation is also the first step in debonding two solid surfaces across a layer of pressure-sensitive adhesive.

Perfect polymer network "specimens" with the chemical constitution of polyethylene, consisting of monodisperse subchains terminally linked at tetrafunctional crosslink points with no dangling ends, have been prepared and fully characterized mechanically under tension/compression via MD simulations.   The specimens have been subjected to hydrostatic tension computer experiments at various levels of stress (negative pressure) [13]. They have been found to cavitate at a stress level, $-P_{cav}$, which is somewhat lower than the limit of mechanical stability, $-P_s$, of the rubbery polymer and of the corresponding linear melt. Analysis of the time to cavitation reveals a nucleation process involving the formation of a critical cavity in unstable mechanical equilibrium, through density fluctuations in the material.

Upon unloading a cavitated specimen, hysteresis is observed on the pressure-specific volume diagram. The volume of the cavitated specimen decreases as the hydrostatic stress is reduced, cavities coalescing into a single spherical cavity which snaps closed at a characteristic stress level $-P_{cl}$, considerably lower than $-P_{cav}$ (see Figure 4). Repeating the loading and unloading experiment in a cyclic fashion causes the material to retrace the loading path of its homogeneous state on the pressure-volume diagram, cavitate at P_{cav} , then trace the unloading path of its cavitated state, and snap back closed at P_{cl}. The isothermal behaviour is thus entirely analogous to a van der Waals loop associated with a first-order phase transition between a homogeneous and a cavitated phase.

The closure stress, $-P_{cl}$, i.e., the stress below which a pre-existing cavity cannot survive within the material, is commensurate with the Young's modulus of the rubber, E. It is entirely comparable to the critical stress anticipated by A.N. Gent and collaborators [14] on the basis of continuum mechanical arguments. Gent et al. considered a pre-existing spherical cavity within a material exhibiting nonlinear large-deformation elasticity following the neo-Hookean equation of state and showed that the cavity will start growing without limit at a critical stress of $5E/6$. The actual values of $-P_{cl}$ in the perfect networks subjected to MD simulation are very close to this critical stress. Furthermore, upon increasing the subchain length in the material, $-P_{cl}$ decreases, remaining commensurate with E, which decreases due to the smaller crosslink density.

Performing the loading and unloading computer experiments at different temperatures T reveals opposite temperature dependences for the cavitation stress $-P_{cav}$ and for the closure stress $-P_{cl}$. The cavitation stress $-P_{cav}$ decreases upon increasing T and depends mainly on the cohesive energy

density of the material. On the contrary, the closure stress $-P_{cl}$ increases upon increasing T, reflecting the entropy elasticity associated with stretching the subchain conformations, and paralleling the behaviour exhibited by the Young's modulus E.
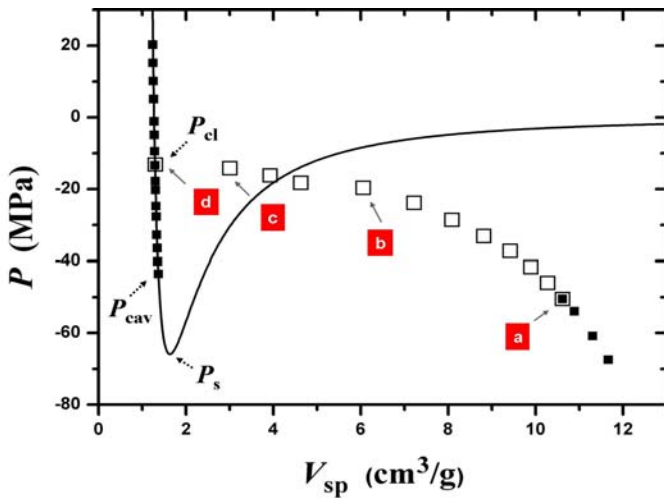
(a)
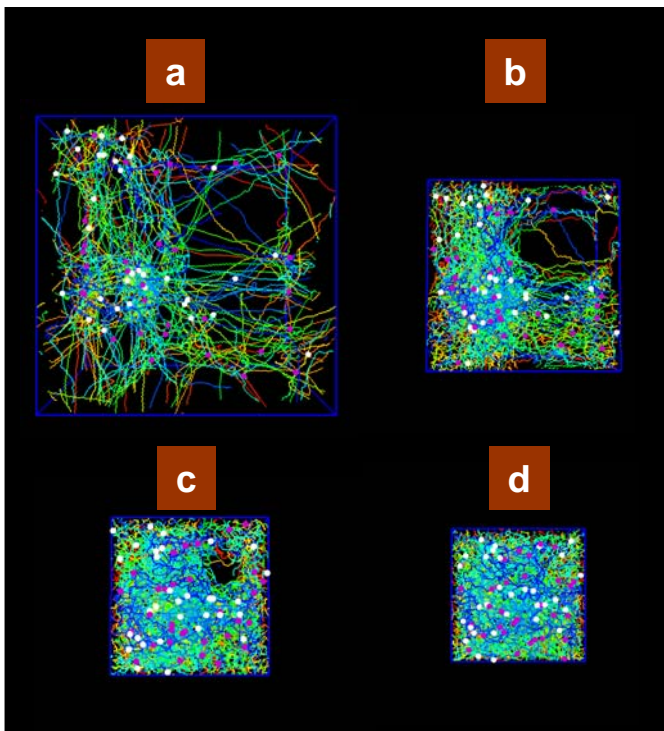
(b)

Figure 4: *(a) Pressure as a function of specific volume for a computer specimen of a perfect tetrafunctional polyethylene network consisting of end-linked 201 carbon-long subchains subjected to hydrostatic tension experiments at 450 K. Bonds are not allowed to break in the model. Simulation points for loading and unloading are shown with filled and open symbols, respectively. The solid line is a fit of the homogeneous (uncavitated) data with the Sanchez-Lacombe equation of state. The (negative) pressure levels P_{cav}, P_{cl}, P_s are indicated. Hysteresis and a van der Waals loop consisting of a homogeneous (left) and a cavitated (right) branch are evident. (b) Snapshots of the specimen at characteristic points marked in (a).*

THE CHALLENGES AHEAD

Thermodynamics-based strategies, such as the ones outlined above, can be invoked within multiscale simulation schemes to predict equilibrium structure and properties of polymeric materials. Moreover, they can be used to relate generator functions and parameters appearing in nonequilibrium thermodynamic formulations for the temporal evolution of material systems, such as GENERIC [15]. Typically, one chooses a set of slowly evolving variables and invokes a time scale separation, assuming that all remaining variables distribute themselves according to the requirements of equilibrium, subject to the constraints imposed by the slow variables. Molecular simulations can then provide the "potential of mean force" (pomf) as a Gibbs or Helmholtz energy that is a function of the slow variables and will dictate their evolution.

Often dynamics is slow because the system has to overcome high (relative to k_BT) barriers in the pomf in order to move from one basin of the pomf ("state") to another in the space of slow variables. The dynamics then acquires the character of a sequence of infrequent jumps between states, successive jumps being practically uncorrelated. Rate constants, i.e., probabilities per unit time, for the jumps to occur can be computed from atomic-level information via the theory of infrequent events. The evolution of the system can then be tracked via solution of a master equation in the occupancy probabilities of the states [16].

Coarse-graining is necessary and basic tools for its implementation are in place. There is still a lot to do, however, to make coarse-graining a generally applicable strategy, subject to minimal loss of information as one passes between different levels of description. For one thing, the choice of slow variables requires a lot of good judgement, which can often be developed by analysis of atomistic simulation trajectories.

In polymers a popular mode of coarse-graining is to group multi-atom moieties into single quasi-atomic entities ("superatoms"). As the pomf with respect to the superatoms is highly multidimensional, approximate expressions are postulated for it, which typically break it up into bonded and nonbonded effective potentials analogous to the ones invoked by atomistic force fields. These contributions can be accumulated in numerical form by iteratively matching intra- and intermolecular correlation functions between atomistic and coarse-grained simulations. This strategy, Iterative Boltzmann Inversion (IBI) [17], has worked well for polymer melts. IBI effective potentials, however, are thermodynamic state-dependent and cannot be used for temperatures, densities, and compositions far from the ones for which they have been accumulated. Using them across phase boundaries is especially unreliable.

Many systems do not reach equilibrium over ordinary time scales. The description of their properties must necessarily be time-dependent. On the other hand, in some of these systems it is not at all obvious how one should define slow variables. A typical example is glasses, which are ubiquitous in the polymer field. Their structure and properties depend on the history of their formation and change with time in the course of physical ageing. Their mechanical response is complex and rate-dependent. "Energy landscape-based" descriptions

are promising for the prediction of glassy dynamics. The molecular configuration is viewed as undergoing infrequent transitions between basins constructed around local minima of the potential energy, the paths and rate constants of each transition being computed by atomistic transition-state theory and the overall evolution of the system being tracked by a master equation. At long times, lumping basins into "metabasins" is necessary, in order to keep the description tractable [16].

Predicting the ultimate mechanical behaviour of polymeric materials is another major challenge for multiscale simulation. Crack propagation typically involves bond breaking, i.e., chemical phenomena, and calls for electronic structure calculations, or refined "reactive force fields". On the other hand, damage zones are large in extent, due to the relative softness of polymeric materials, and the constitutive behaviour around crack tips may be highly viscoelastic. The state of the art in simulating fracture of primarily nonpolymeric materials has been summarized [18].

NOMENCLATURE

Symbol	Quantity	SI Unit
E	Young's modulus	Pa
H'	Weight fraction-based Henry's law constant	Pa
$\mathbf{k}$	Wave vector	m^{-1}
k_B	Boltzmann's constant	$J\,K^{-1}$
M	Number average molar mass of chains	$kg\,mol^{-1}$
M_e	Molar mass between entanglements	$kg\,mol^{-1}$
n	Degree of polymerization, measured in repeat units	-
P	Pressure	Pa
P_{cav}	Cavitation pressure of rubbery polymer	Pa
P_{cl}	Closure pressure of rubbery polymer	Pa
P_s	Limit of mechanical stability, i.e. pressure at which the isothermal slope of pressure with respect to specific volume becomes zero.	Pa
$\langle R^2 \rangle$	Mean squared end-to-end distance of a chain	m^2
S	Static structure factor for X-ray diffraction	-
T	Absolute temperature	K
T_m	Equilibrium melting point	K
V_{sp}	Specific volume	$m^3\,kg^{-1}$
λ	Parameter in artificial potential inducing helical conformation of chains	-

REFERENCES

[1] see, for example, P. Nielaba, M. Mareschal, and G. Ciccotti (eds.) *Bridging Time Scales: Molecular Simulations for the Next Decade*, Springer, Heidelberg, 2002.

[2] C.E. Wilmer, M. Leaf, C.Y. Lee, O.K. Farha, B.G. Hauser, J.T. Hupp, and R.Q. Snurr, Large-scale Screening of Hypothetical Metal-organic Frameworks for Methane Storage, *Nature Chemistry*, vol. 4, pp. 83-89, 2012.

[3] see, for example, M. Wilson, M. Allen, G. Jackson, S. Marrink, M. Sansom, and D. Theodorou (eds.) *Multiscale Modelling of Soft Matter*, *Faraday Discussion, Vol.* 144, RSC Publishing, 2010.

[4] R.O. Dror, R. M. Dirks, J.P. Grossman, H.Xu, and D.E. Shaw, Biomolecular Simulation: A Computational Microscope for Molecular Biology, *Annual Review of Biophysics*, vol. 41, pp. 429–452, 2012.

[5] D.N. Theodorou, Variable Connectivity Monte Carlo Algorithms for the Atomistic Simulation of Long-Chain Polymer Systems, in P. Nielaba, M. Mareschal, and G. Ciccotti (eds.) *Bridging Time Scales: Molecular Simulations for the Next Decade*, chap. 3, Springer, Heidelberg, 2002.

[6] C. Tzoumanekas and D.N. Theodorou, Topological Analysis of Linear Polymer Melts: A Statistical Approach, *Macromolecules*, vol. 39, pp. 4592-4603, 2006.

[7] K. Moorthi, K. Kamio, J. Ramos, and D.N. Theodorou, Monte Carlo Simulation of Short-chain Branched Polyolefins: Structure and Properties" *Macromolecules,* vol. 45, pp. 8453-8466, 2012.

[8] B. Widom, Some Topics in the Theory of Fluids, *J. Chem. Phys.*, vol 39, pp. 2808-2812, 1963.

[9] G.C. Boulougouris, I.G. Economou, D.N.Theodorou, On the Calculation of the Chemical Potential Using the Particle Deletion Scheme, *Molec. Phys.*, vol. 96, pp. 905-913, 1999.

[10] M.G. De Angelis, G.C. Boulougouris, and D.N. Theodorou, Prediction of Infinite Dilution Benzene Solubility in Linear Polyethylene Melts via the Direct Particle Deletion Method, *J. Phys. Chem. B,* vol. 114, pp. 6233-6246, 2010.

[11] T. Spyriouni, G.C. Boulougouris, and D.N. Theodorou, Prediction of Sorption of CO_2 in Glassy Atactic Polystyrene at Elevated Pressures Through a New Computational Scheme, Macromolecules, vol. 42, pp 1759-1769, 2009.

[12] A. Romanos and D.N. Theodorou, Crystallization and Melting Simulations of Oligomeric α1 Isotatic Polypropylene, Macromolecules, vol. 43, pp. 5455-5469, 2010.

[13] A. K. Morozinis, C. Tzoumanekas, S.D. Anogiannakis, and D. N. Theodorou, Atomistic Simulations of Cavitation in a Model Polyethylene Network, Polymer Science, Ser. C, vol. 55, 2013, in press.

[14] A.N. Gent and P.B. Lindley, Internal Rupture of Bonded Rubber Cylinders in Tension, Proc. Roy. Soc. (Lond.), vol. A249, pp. 195-205, 1958.

[15] H.C. Öttinger, *Beyond Equilibrium Thermodynamics*, Wiley, 2005.

[16] D.N. Theodorou, Tracking the Dynamics of Systems Evolving through Infrequent Transitions in a Network of Discrete States, in J. Grotendorst, G. Sutmann, G. Gompper, and D. Marx (eds.) *Hierarchical Methods for Dynamics in Complex Molecular Systems,* Schriften des Forschungzentrums Jülich, IAS Series volume 10, pp 347-389, Jülich , 2012.

[17] D. Reith, M. Pütz, F. Müller-Plathe, Driving Effective Mesoscale Potentials from Atomistic Simulations, *J. Comp. Chem.,* vol. 24, pp. 1624-1636, 2003.

[18] M.J. Buehler, *Atomistic Modeling of Materials Failure*, Springer, New York, 2008.