Grant Number: DE-SC0002011 to the University of Delaware

Title of Award: "Nanoparticles Stabilize Thin Polymer Films: A Fundamental Study to Understand the Phenomenon"

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Dr. Amalie Frischknecht – Sandia National Laboratories
Dr. Venkat Padmanabhan– Postdoctoral Associate
Mr. Wenluan Zhang – Graduate Student

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Final report

Project organization

In this project we have successfully married an experimental – theoretical collaboration between the University of Delaware research group and Sandia National Laboratories. To do this Prof. **Mackay** supervised graduate students, Ms. Erica Tzu-Chia **Tseng** and Mr. Wenluan **Zhang**, who performed experiments, and a postdoctoral fellow, Dr. Venkat **Padmanabhan**, who performed theoretical modeling in his laboratory and interacted with Dr. Amalie **Frischknecht**, a theoretician at SNL. Drs. **Padmanabhan** and **Frischknecht** had weekly teleconferences on Tuesday mornings to discuss progress and had 2-3 face-to-face meetings per year. Dr. **Frischknecht** was funded on her part through **CINT** to allow this partnership. This unique collaborative effort of placing a theoretician within a group of experimentalists has tremendously aided experimental progress since the collaborators are intimately familiar with both the experimental and theoretical efforts. Furthermore development of new theoretical tools to interpret experimental results has resulted in rational verification and enhanced investigation of parameter space.

Summary of accomplishments

Accomplishment 1 - It is well known that a mixture of big and small hard spheres next to a planar wall will exhibit segregation based on their size difference. The larger spheres will tend to locate next to the substrate because the overall system entropy loss per unit area is less. We have determined the role of attraction between the small particles and the wall to displace the larger particles. Both fluids density functional theory and discontinuous molecular dynamics simulations demonstrate that at a certain attractive potential, which is on the order of the thermal energy, the large particles can indeed be dislodged from the surface layer so the small particles are now the major surface component. Exploration of a range of parameters, including relative sphere size and concentration, as well as attractions between the small spheres in the bulk, shows that the phenomenon is quite robust.

Accomplishment 2 - We extend the above work to investigate the phase behavior of polymer/nanoparticle blends near a substrate using fluids density functional theory with mean-field attractions. The blends are modeled as a mixture of spherical particles and freely jointed chains near a planar wall. The attractive interactions, both for nanoparticle/polymer and polymer/wall are given by an exponential form. Earlier studies have shown that for an athermal system, there is a first order transition, where the nanoparticles expel the polymer from the surface to form a monolayer at a certain nanoparticle concentration. This transition has been justified by nanoparticle segregation to the substrate observed in experiments. In the presence of attractions, the first order transition moves to higher nanoparticle concentrations as the strength of attraction is increased. Our results show that the transition is prevented at very high attractions.

Accomplishment 3 - Molecular dynamics simulations have been employed to study the effect of chain stiffness in polymer/nanoparticle blends near a substrate. The nanoparticles are modeled as spheres of diameter σ_n and the polymers are modeled as bead-spring chains using the finite extensible nonlinear elastic (FENE) potential with a bead diameter σ_p. The stiffness of these chains is controlled by a cosine potential that limits the angle between two consecutive bonds. The non-bonded interactions are given by the Lennard-Jones potential. Our earlier theoretical studies, using the fluids density functional theory for blends with freely jointed chains, showed that there is a first order transition, where the nanoparticles expel the polymer from the surface to form a monolayer at a certain nanoparticle concentration. The location of this transition depends on the type of interaction and its strength. In this work using MD simulations, we find no such sharp phase transition. However, the nanoparticles do migrate to the surface at higher volume fractions. Our results indicate that for a fixed volume fraction of nanoparticles in the blend, when the chains are made stiffer, the surface density of polymers increases and the surface density of nanoparticles decreases.

Accomplishment 4 – We have successfully assembled nanoparticles around a larger particle in a thin film and in the bulk. This is based on our theoretical observations discussed above and previous experimental results and is important since it can be used in a variety of applications including making new three-dimensional band structures and for application in polymer-based solar cells. This is an exciting new avenue of nanoparticle assembly processes.

Accomplishment 1 – Binary fluid of two different sized spheres with attractions near a planar wall

We use classical density functional theory (DFT) to study a mixture of binary fluids near a smooth wall. DFT has been shown to very accurately describe the statistical mechanics of hard spheres[1] and hard sphere mixtures near surfaces[2]. The DFT accurately captured the depletion effects for these mixtures, for three different versions of the Rosenfeld density functional. In this work, we use the "White-Bear" functional[3] that provides slightly more accurate density profiles, especially near contact, of hard sphere mixtures near a planar hard wall. We verify the accuracy of the DFT for our binary mixtures with small particle-wall attractions by also performing discontinuous molecular dynamics (MD) simulations on the same systems. We study the effects of attractions between the small particles by combining the hard-sphere White-Bear functional with a mean-field description of the attractions.

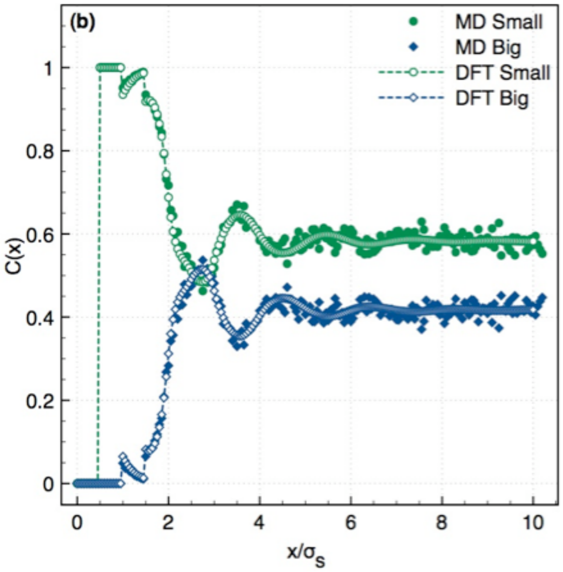

Figure 1. Concentration profiles for the small (green circles) and large (blue diamonds) particles with ε_{wf} = 2.0 and η_s = 0.060.

The generic methodology of classical DFT is built upon a mathematical theorem stating that in an open system specified by temperature *T*, total volume *V*, and chemical potentials of all constituent molecules μ_i, there is an invertible mapping between the external potential and the one-body density profiles[4,5,6,7]. In other words, there exists a density distribution $\rho_i(\mathbf{r})$ of the constituent species *i* that minimizes the functional $\Omega[\rho_i]$. This minimization is performed using a variational approach, while keeping chemical potential μ_i, volume *V*, and temperature *T*, constant. This functional corresponds to the grand potential Ω of an open (μVT) ensemble.

An example of the concentration profiles is shown in Figure 1 for a small sphere – wall interaction energy of 2.0 (ϵ_{wf} = 2.0). These concentration profiles demonstrate that for a stronger wall-small particle attraction, the enthalpic force due to the attraction between the small spheres and the wall dominates over the entropic force, resulting in the small spheres replacing the big spheres at the wall. This is clearly seen in Figure 1, where the concentration of the small spheres is much higher than the concentration of the big spheres near the wall. The concentration of small and big spheres near the surface as a function of wall-fluid attractions is shown in Figure 2.

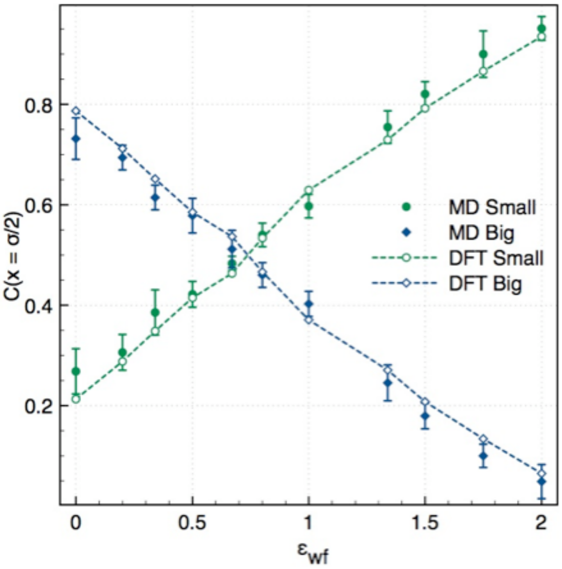

Figure 2. Concentrations of big (blue diamonds) and small (green circles) spheres near the wall, for $\varepsilon_{ff} = 0$, $\xi = 2$, and $\Phi_s \approx 0.22$. The increasing curve is for small spheres and the decreasing curve is for big spheres.

Accomplishment 2 – Phase behavior of polymer/nanoparticle blends with attractions near a substrate

In blends of nanoparticles and homopolymers near substrates, the nanoparticles often segregate to the substrate upon annealing. This has been seen experimentally in several systems, including polystyrene (PS) nanoparticles[8], cadmium selenide (CdSe) quantum dots[9], and buckyballs blended with PS[10], and in mixtures of PS-coated gold nanoparticles in PS[11,12]. In the first case of PS nanoparticles in PS, the interactions in the blend are predominately entropic because of the chemical similarity of the nanoparticles and polymer. The segregation of the nanoparticles in this case is due to packing entropy effects from the asymmetry in sizes between the two constituents as well as to polymer configurational entropy loss near the substrate[12]. For the other systems, the self-assembly is controlled by the interplay between surface energies, dispersion forces and entropy.

Here, we explore how variations to the system affect the presence of the first-order transition found in our previous work[13,14], hereafter referred to as Paper 1 and Paper 2, respectively. The calculations in Papers 1 and 2 assumed that the total packing fraction of the system remained constant as nanoparticles were added. This is a natural assumption to make in a DFT, which is formulated in an open ensemble specified by chemical potential, temperature and volume. The chemical potentials are determined by the bulk densities far from the substrate, so the most straightforward way to do the calculations is to directly specify the chemical potentials through the bulk densities, i.e. the packing fractions. However, experimental systems are usually at constant pressure. Here we consider the calculations of Papers 1 and 2 at constant pressure. We still find a first-order transition, but with some differences as described below. In addition, although not discussed here, we examined the effects of attractions on the system, also at constant pressure. We find that adding an attractive monomer-nanoparticle interaction increases the number of nanoparticles required to induce the phase transition, and that for sufficiently large attractions the first-order transition disappears. We also considered an attractive polymer-substrate attraction in the otherwise hard sphere system.

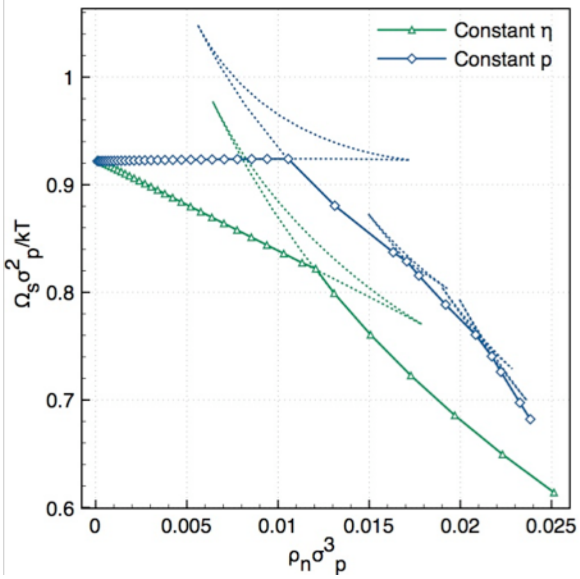

Figure 3. Surface free energy as a function of nanoparticle density for a system with N = 80 and $\sigma_n = 2\sigma_p$. Open squares correspond to constant pressure and open triangles correspond to constant packing fraction calculations.

Figure 3 shows the surface free energy as a function of nanoparticle density for chains with length, N = 80 and particles with diameter, $\sigma_n = 2\sigma_p$ for both the constant p and constant η cases. The butterfly-shaped curve shows the entire path traced by the solver starting from the low-density stable branch, which is highlighted with symbols and the metastable regions indicated by dotted lines. Notice that the surface free energy decreases in the constant η case while it increases in the constant p case as we increase the nanoparticle concentration. The higher free energy in the case of constant pressure calculations is related to the increase in the number density as more nanoparticles are added. The entire surface free energy plot is traced as follows: First, a solution is found with a low concentration of nanoparticles. An arc-length continuation algorithm is then started with an initial step in the direction of increased nanoparticle density. The algorithm finds new solutions by taking (adaptable) steps along the solution branch as a function of $\rho_n\sigma_n^3$ and reconverging from previous solution. The curve is traced until the spinodal point is reached on the far right of the figure. The solver detects no solutions to the DFT equations beyond this point and hence turns around and continues along an unstable branch of the curve until it reaches the second spinodal point at the top of the figure. Again, there are no more solutions beyond this point. So, the solver takes a downturn and crosses previous results and continues downward. The parts of the curve with the lowest free energies represent the equilibrium states of the system and are marked with symbols. The distinct change in slope at the crossing point indicates a first order phase transition; the transition points at $\rho_n^* = 0.01056$ and 0.01207 for the constant p and constant η cases respectively are the binodal points. Note that the number of nanoparticles, in the constant p case, required to induce the transition is smaller. At these points there are two distinct solution morphologies with the same free energy that coexist. There are two solutions on either side of the phase transition; the stable equilibrium one and the metastable branch.

Accomplishment 3 – Effect of chain stiffness on nanoparticle segregation in polymer/nanoparticle blends near a substrate

In our previous work on polymer/nanoparticle blends near the surface using fluids DFT, we considered attractive systems with two different kinds of attractions – polymer/nanoparticle and polymer/surface attractions. In both these cases, the first order transition was observed but shifted depending on the strength of attractions. However, for very high attractions, the enthalpic force in the system dominates over the entropic forces and completely prevents the segregation of nanoparticles to the surface. In the polymer/nanoparticle attraction case, for very strong attractions, the free energy of mixing dominates over the entropic forces and in the polymer/surface attraction case, the enthalpic force between the polymers and the surface dominates.

In the above-mentioned work, the polymers were modeled as a freely jointed chain. However, in the real world, different polymers have different degrees of stiffness in their backbone. In order to thoroughly understand the role of chain stiffness on the nanoparticle segregation to the substrate, we use molecular dynamics (MD) simulations on a simplified model system. When the chains are stiffer, the constraint imposed by the substrate on possible conformations is significantly reduced. This has a huge effect on the entropically driven segregation of nanoparticles. Chains with limited flexibility have shown the tendency to form liquid crystalline domains at high densities[15,16,17,18,19]. However, this first order transition from an isotropic to a nematic phase is observed only when the chain stiffness is greater than a certain minimum value[20,21,22,23]. In this work, we consider chains with stiffness below this value and hence do not see any nematic ordering in our systems. The stiffness is graded by the bending energy parameter, K, with a larger K meaning a stiffer chain.

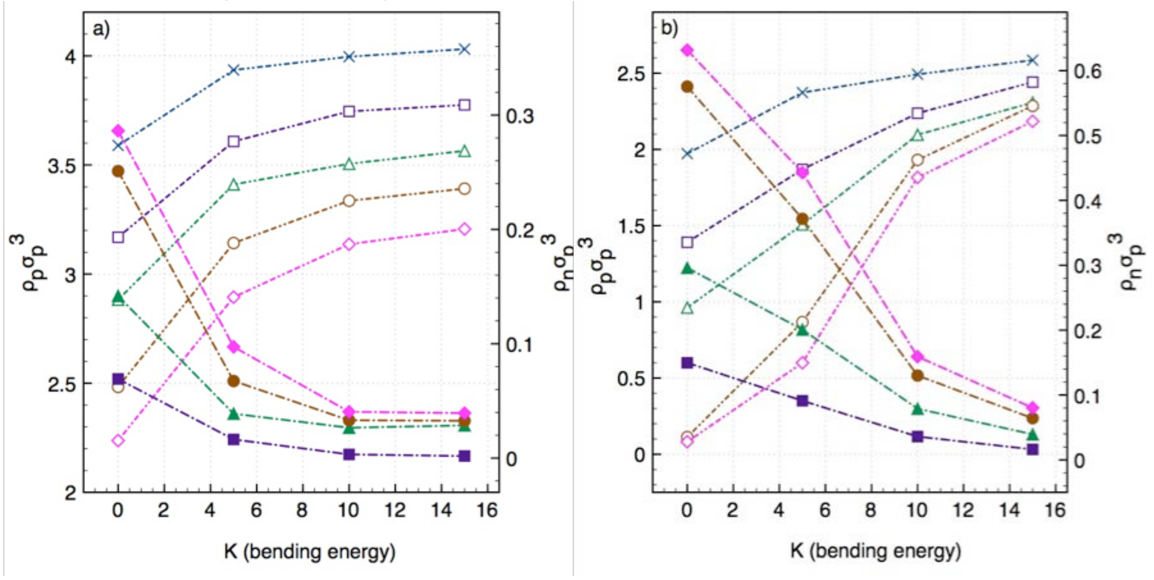

Figure 4. Densities near surface as a function of K for (a) purely repulsive and (b) attractive system. Solid symbols – NPs, Open symbols – polymer with markers: X ➔ $\Phi_{np} = 0$, ☐ ➔ $\Phi_{np} = 7$, Δ ➔ $\Phi_{np} = 13$, **O** ➔ $\Phi_{np} = 20$, and ◆➔ $\Phi_{np} = 25$

Figure 4 shows the densities of both polymers and nanoparticles close to the surface as a function of K for (a) repulsive (hard sphere) and (b) attractive systems. In order to calculate the densities of both species near the surface, the simulation box was divided into a number of bins along the axis perpendicular to the surface and the number of particles in each bin was counted. The density corresponding to the bin at a distance σ/2 from the surface is the density of that species near the surface. For both systems, we note that at very low values of K, the concentration of nanoparticles near the surface is high. This is attributed to the flexibility of the chains that contribute to the total entropy gain by pushing the nanoparticles close to the surface. When the chains become stiffer, the force pushing the nanoparticles to the surface is reduced because the contribution to the total entropy from the chain configurational entropy is reduced. So, the concentration of nanoparticles close to the surface is lowered with increasing stiffness. We note that the nanoparticle concentration next to the surface decreases asymptotically with increasing stiffness. So, higher values of K (>15) do not show significant change in the density distributions.

Accomplishment 4 – Assembly of nanoparticles around a larger particle

We are very interested in the assembly of nanoparticles in thin polymer films and we have found that it is possible to assemble nanoparticles to either the air interface or to the solid substrate interface. Note these are thermodynamically stable nanoparticles in the bulk and do not normally phase separate. It is the hard substrate that causes them to assemble to it by entropic or enthalpic forces while the air interface causes blooming of the lowest energy component, either the nanoparticle or the polymer, to it. This is an enthalpic force and is driven by dielectric ordering.

If a substrate is placed within the bulk, like a larger colloidal scale particle, will segregation of nanoparticles occur at its boundary? We did some preliminary experiments on this and as shown in Figure 5 the nanoparticles appear to assemble around a larger silica particle. The forces that drive it are most likely due to entropy where the polymer molecule traps it to the larger particle surface. However, there is probably dielectric (van der Waals) attraction of the nanoparticle to the larger particle.

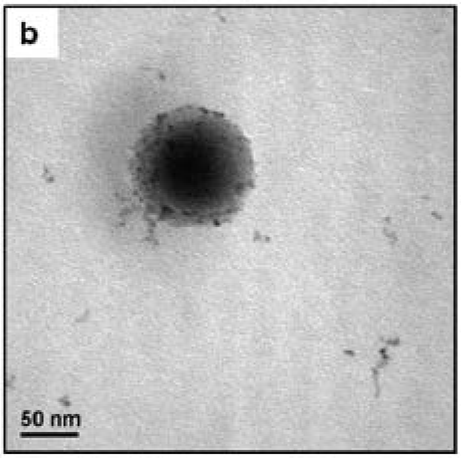

Figure 5. Assembly of quantum dots around a silica particle in polystyrene.

We are presently (experimentally) analyzing the assembly of this and similar systems to understand the assembly process. This has many applications including making new band structures. Imagine nanoparticles surrounding the solid object which are very close together so they form a band structure. Now if they assemble around a spherical particle we will have a spherical band structure which has never been created before. In addition, these structures may have application in polymer-based solar cells which could aid their efficiency in absorption processes, charge separation and charge mobility.

Publications

Published manuscripts

Frischknecht, A. L., McGarrity, E. S., and Mackay, M. E., Expanded chain dimensions in polymer melts with nanoparticle fillers. *J Chem Phys* **132**, 204901 (2010).

Kiel, J.W., Eberle, A.P.R., and Mackay, M.E., Nanoparticle agglomeration in polymer-based solar cells. *Phys Rev. Letters* **105**, 168701 (2010).

Kiel, J. W., Kirby, B. J., Majkrzak, C. F., Maranville, B. B., and Mackay, M. E., Nanoparticle concentration profile in polymer-based solar cells. *Soft Matter* **6**, 641 (2010).

Kiel, J. W., Mackay, M. E., Kirby, B. J., Maranville, B. B., and Majkrzak, C. F., Phase-sensitive neutron reflectometry measurements applied in the study of photovoltaic films. *J. Chem. Phys* **133**, 074902 (2010).

Padmanabhan, V., Frischknecht, A. L., and Mackay, M. E., Binary fluid with attractions near a planar wall. *Phys Rev E* **82** (2010).

Tseng, Tzu-Chia, McGarrity, Erin S., Kiel, Jonathan W., Duxbury, Phillip M., Mackay, Michael E., Frischknecht, Amalie L., Asokan, Subashini, and Wong, Michael S., Three-dimensional liquid surfaces through nanoparticle self-assembly. *Soft Matter* **7**, 1533 (2010).

Frischknecht, A.L., Padmanabhan, V. and Mackay, M.E., Surface-induced phase behavior of polymer/nanoparticle blends with attractions, Journal of Chemical Physics **136** (2012).

Padmanabhan, V., Frischknecht, A.L. and Mackay, M.E., Effect of chain stiffness on nanoparticle segregation in polymer/nanoparticle blends near a substrate, Macromolecular Theory and Simulations **21** (2012) 98-105.

Manuscripts that have been written and are under final revision and partially funded by this grant

n/a

Manuscripts that will be written soon and primarily funded by this grant

W. Zhang, M.E. Mackay, B.J. Kirby, B.D., Maranville, and C.F. Majkrzak, Nanoparticle concentration profile in PBTTT thin film solar cells.

People who worked on this project

All personel were funded 100% by this grant and worked 100% on this project. The exception is Dr. Frischknecht who is an employee of Sandia National Laboratories. Her research was supported by CINT and she collaborates with us on this project.

Graduate students – Erica Tseng (finished in July 2010)
Wenluan Zhang (started Jan 2010)

Postdoc - Dr. Erin S. McGarrity (ended February 2009)
Dr. Venkat Padmanabhan (started March 3, 2009)

Collaborator - Dr. Amalie Frischknecht, Sandia National Laboratories & CINT

Relationship of this award to other awards

The research in this award is independent of research carried out in other awards.

Current and Pending Support

Current

70NANAB10H256 09/1/2010 - 8/31/2015 1.0 Summer Month
National Institutes of Health $3,662,127 (Lead PI, Wagner)
Advanced metrology using USANS, in support of sustainable energy, health, and nanomaterials research
Role: Co-PI

Pending

Univ. of Arizona/NSF 07/01/2013 – 06/30/2014 .25 Summer Month
$73,027
Polymerization of Elemental Sulfur to Prepare Electroactive Copolymers for Li-S Batteries
Role: PI

Vanderbilt Univ/NSF 05/01/2013 – 04/30/2016 .125 Academic Month
$120,000
Synthesis of Functionalized Polyester and Polycarbonate Nanosponges and Investigation of the Structure Property Relationship
Role: PI

NASA 11/01/2013 – 10/31/2016 1.0 Summer Month
$749,160 (Lead PI, Dermott Mullan)
Design and Fabrication of Novel Optical Lenses for Space Applications
Role: Co-PI

Biosketch
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Education:

Ph.D.in Chemical Engineering, 1985, University of Illinois – Urbana-Champaign,
Advisor: Prof. A.J. McHugh, Thesis: ‘Behavior of polymer solutions and melts in shearing and elongational flow using streak photography and birefringence’

M.S.in Chemical Engineering, 1983, University of Illinois – Urbana-Champaign,
Advisor: Prof. A.J. McHugh, Thesis: ‘Converging flow of a Newtonian fluid in a film extrusion geometry’

B.S. in Chemical Engineering (with distinction), 1979, University of Delaware
Advisor: Prof. M.E. Paulaitis, Thesis: ‘Optimal representation of vapor-liquid equilibria’

Professional Experience:

2009–Present	Distinguished Professor of Materials Science and Engineering, Univ. Delaware
2008–Present	Professor, University of Delaware
2001–2008	Professor, Michigan State University
1999–2001	Professor, Stevens Institute of Technology
1994–1998	Associate Professor, Univ. Queensland (U.S. equivalent – Professor)
Fall 1994	Visiting Professor, Univ. Delaware
1991–1994	Senior Lecturer, Univ. Queensland (U.S. equivalent – Associate Professor)
Fall 1990	Visiting Professor, Cambridge Univ.
1987–1991	Lecturer, Univ. Queensland (U.S. equivalent – Assistant Professor)
1985–1987	Postdoctoral Fellow, Univ. Melbourne
1979–1980	Staff Engineer, Procter and Gamble

Selected Publications:

1. J. Kiel, B. Kirby, C. Majkrzak, B. Maranville and M. E. Mackay, "Nanoparticle concentration profile in polymer-based solar cells," Soft Matter **6** (2010) 641-646.
2. J. Kiel, M.E. Mackay, B. Kirby, B. Maranville and C. Majkrzak, “Phase-sensitive neutron reflectometry measurements applied in the study of photovoltaic films,” J. Chem. Phys. **133** (2010) 074902.
3. Kiel, J.W., Eberle, A.P.R., and Mackay, M.E., Nanoparticle agglomeration in polymer-based solar cells. Phys Rev. Letters **105**, (2010) 168701.
4. Burattini, S.; Colquhoun, H. M.; Fox, J. D.; Friedmann, D.; Greenland, B. W.; Harris, P. J. F.; Hayes, W.; Mackay, M. E.; Rowan, S. J., “A self-repairing, supramolecular polymer system: healability as a consequence of donor-acceptor pi-pi stacking interactions,” Chem. Comm. **44** (2009) 6717-6719.
5. E. S. McGarrity, A. L. Frischknecht, L. J. D. Frink and M. E. Mackay, "Surface-induced First Order Transition in Athermal Polymer/Nanoparticle Blends," Phys Rev Letters, **99** (2007) 238302-1 - 4.
6. R. S. Krishnan, M. E. Mackay, P. M. Duxbury, A. Pastor, C. J. Hawker, B. Van Horn, S. Asokan and M. S. Wong, "Self-assembled multilayers of nanocomponents," Nano Letters, **7** (2007) 484-489.
7. A. Tuteja, M. E. Mackay, S. Narayanan, S. Asokan and M. S. Wong, "Breakdown of the continuum Stokes-Einstein relation for nanoparticle diffusion," Nano Letters, **7** (2007) 1276-1281.
8. M. E. Mackay, A. Tuteja, P. M. Duxbury, C. J. Hawker, B. V. Horn, Z. Guan, G. Chen and R. S. Krishnan, "General Strategies for Nanoparticle Dispersion," Science, **311** (2006) 1740-1743.
9. S. Sivakova, D. A. Bohnsack, M. E. Mackay, P. Suwanmala and S. J. Rowan, "Utilization of a Combination of Weak Hydrogen-Bonding Interactions and Phase Segregation to Yield Highly Thermosensitive Supramolecular Polymers.," J. Am. Chem. Soc, **127** (2005) 18202-18211.
10. Mackay, M. E., T. T. Dao, A. Tuteja, D. L. Ho, B. van Horn, H.-C. Kim and C. J. Hawker, "Nanoscale effects leading to non-Einstein-like decrease in viscosity," Nature Materials **2** (2003) 762-766.

Synergistic Activities:

1. Developed and taught a course in Solar Energy and is currently writing a book on the topic for Oxford University Press
2. Organizer with Profs. J. Sommer and M. Stamm of the “Polymer Nanoparticle Interactions” W.E. Heraeus Seminar, 28-31 March 2010 at the Physikzentrum Bad Honnef, Germany
3. Session chair and organizer for “Polymeric Nanostructures” session at Chicago 2007 ACS Meeting (with Prof. Stuart Rowan and Dr. Amalie Frischkneckt).
4. Presented a 3 day course on Nanoscale Characterization at The University of Queensland in August 2 – 4, 2006.
5. Given presentations to elementary school children on nanotechnology several times.

Graduate students:
Ph.D (32 supervised in total): D. Bohnsack (2007) TA Instruments, T. Bohnsack (2007) Henkel, M. Holmes (2007) Sandia, Jon Kiel (2010) Postdoc-Stanford U, R.S. Krishnan (2006) Intel, L. Passeno (2006) Sika, Jon Seppala (2010) Postdoc-Delaware, A. Tuteja (2006) Prof. U Mich, Erica Tseng (2010) Postdoc-CA

MS (2 supervised)*:* Glenda Carmezini (2000), J. Sutton (2003)

Presently supervising: Brett Guralnick (ChE), Robert Jones (MSE), Ngoc Ahn Nguyen (MSE), Rodell Remy (MSE), Hao Shen (ChE), Jeong Jae Wie (ChE), Wenluan Zhang (MSE)

Postdoctoral Researchers: (*9 supervised in total)*
Kailash Awati (1997-9), Tien D. Dao (2001-3), Donia Freidman (2008), Peter Halley (1994-5) Univ. Qld., Ye Hong (1998-9), Camilla Kelly (1995-8), Erin McGarrity (2005-7), Venkat Padmanabhan (2009–present), Eric Weisser (1996-8), Wengui Weng (2009)

Collaborators:
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Recent Collaborators: G. Baker (MSU)**,** H. Colquhoun (Reading U), P. Duxbury (MSU), A. Frischnechkt (Sandia), C. Hawker (UCSB), W. Hayes (Reading U), J Loos (U Glasgow), D. Pochan (UD), J. Pyun (U Arizona), S. Rowan (CWRU), N. Wagner (Delaware), M.S. Wong (Rice U), K.L. Wooley (Texas A&M)

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