
This month Schweizer published a theory for the mechanical properties of polymer nanocomposites (NC) (Zhou Y, Schweizer KS *Theory for the Elementary Time Scale of Stress Relaxation in Polymer Nanocomposites* ACS Macro Lett. 11 199-204 (2022)). Zhou’s paper deals with the interaction between nanoparticles, \( \varepsilon_{np} \), in a polymer NC that was mentioned by Mackay in Mackay ME, Tuteja A, Duxbury PM, Hawker CJ, Van Horn B, Guan Z, Chen G, Krishnan RS *General Strategies for Nanoparticle Dispersion* Science 311 1740-1743 (2006) as shown in Mackay’s Figure 3, specifically the brown disks which reflected van der Waals interactions for Mackay. Zhou considers that, under the conditions of strong polymer/NP interaction, large \( \varepsilon_{pm} \), this brown disk is composed of polymer chain units/beads of size \( \sigma \), shown as green dots in Zhou’s Figure 1. Large \( \varepsilon_{pm} \) also leads to clusters of NPs rather than a uniform distribution. The system colloidal silica–P2VP (poly2vinylpyridine) displays such large \( \varepsilon_{pm} \). Experimental scattering data can be used to determine the parameters needed for the PRISM simulation.

MacKay’s Figure 3. Zhou’s Figure 1. P2VP. Graphical Abstract Zhou, Yavitt et al.(2020)

a) Zhou’s Equation 1 indicates that the relaxation time associated with nanoparticle binding has two components, one associated with the polymer matrix (grey in Zhou’s Figure 1) and one that has an Arrhenius thermal dependence that is associated with the energy \( \Delta E \) of binding for the green dots in Zhou’s Figure 1.

\[ \tau_{\text{theo}}(T) \approx \tau_{\text{poly}}(T)e^{\beta \Delta E} \]

\( \Delta E \) is the “…activation energy for bridging complex relaxation based on viscoelastic data, the microscopic origin of which is not known.”. Zhou seeks to define the origin of and calculate the value for this activation energy in his proposed model. Zhou proposes that
$\Delta E \approx n_B \Delta w$ \ where \ $n_B$ \ is \ the \ number \ of \ green \ dots \ in \ his \ Figure \ 1 \ and \ $\Delta w$ \ is \ the \ NP \ “potential-of-mean \ force (PMF) \ barrier”. \ Explain \ the \ origin \ of \ the \ Arrhenius \ function \ and \ what \ type \ of \ systems \ it \ is \ intended \ to \ model. \ Is \ this \ function \ appropriate \ for \ Zhou’s \ model?

b) \ Figure \ 2a \ shows \ a \ plot \ of \ the \ nanoparticle-nanoparticle \ correlation \ function \ obtained \ from \ PRISM \ using \ experimental \ parameters \ versus \ the \ separation \ distance \ of \ nanoparticles \ normalized \ by \ the \ polymer \ bead \ size. \ $D$ \ is \ the \ nanoparticle \ size, \ $D = 10 \sigma$. \ Explain \ why \ two \ prominent \ peaks \ are \ seen, \ why \ the \ first \ peak \ only \ occurs \ at \ high \ NP \ concentration. \ What \ is \ $r_m$? \ Why/how \ is \ it \ used \ to \ determine \ $n_B$ \ from \ the \ equation \ in \ question \ “a”. \ How \ is \ $\Delta w$ \ from \ that \ equation \ determined?

c) $n_B, \Delta w, \text{and} \Delta E \text{ show interesting non-linear behavior in concentration, Figure 3.} \ Why \ does \ the \ number \ of \ beads \ in \ Figure \ 1 \ increase \ with \ concentration? \ Why \ does \ the \ potential \ of \ mean \ force \ decrease? \ Why \ does \ the \ activation \ energy \ increase? \ The \ curves \ are \ normalized \ in \ the \ insets \ to \ Figure \ 3. \ Explain \ the \ reasoning \ behind \ each \ of \ the \ three \ insets \ to \ Figure \ 3.

d) Figure \ 4 \ compares \ the \ experimentally \ determined \ activation \ energy \ with \ that \ determined \ from \ the \ PRISM \ simulation \ based \ on \ the \ Zhou/Schweizer \ model. \ $\varepsilon_{prism}$ \ is \ varied \ by \ variation \ in \ the \ matrix \ polymer. \ How \ is \ $\Delta E$ \ measured \ experimentally? \ Why \ is \ there \ no \ molecular \ weight \ dependence \ to \ the \ results? \ The \ inset \ to \ Figure \ 4 \ shows \ the \ data \ scaled \ with \ a \ parameter \ $\lambda$ \ which \ has \ a \ value \ of \ 1 \ for \ PVAc, \ 2.1 \ for \ PMMA, \ and \ 5 \ for \ P2VP. \ Speculate \ on \ what \ this \ parameter \ reflects.

e) Zhou Y, Yavitt BM, Zhou Z, Bocharova V, Salatto D, Endoh MK, Ribbe AE, Sokolov AP, Koga T, Schweizer KS Bridging-Controlled Network Microstructure and Long-Wavelength Fluctuations in Silica–Poly(2-vinylpyridine) Nanocomposites: Experimental Results and Theoretical Analysis Macromolecules 53 6984-6994 (2020) study the same P2VP-silica system with SAXS. Their graphical abstract (shown above) shows a discrepancy between the PRISM results for the correlation function and the measured structure factor. Can you explain this difference? How is this discrepancy resolved in Figure 4? What is the packing fraction, $\eta$? (Ben Yavitt has been offered a faculty position in the Materials Program at UC starting in the Fall Semester.)

f) Please comment on the course, specifically:
1) Did you learn something of use?
2) Was the group homework/grading format acceptable?
3) Was the hybrid format useful?
4) Was the format of looking at a current paper rather than going through the lecture content useful?
5) Do you have any suggestions for improvement?