Dynamics of concentrated suspensions of nanoparticles in semidilute polymer solutions

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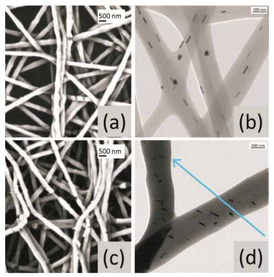
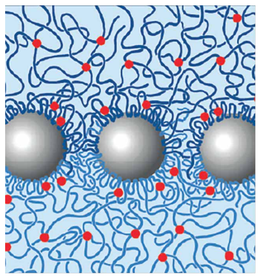
Composites Exhibit Enhanced Properties

- Mechanical properties of nanocomposites are significantly enhanced compared to neat polymer melts
- The dynamic relaxations of particles and polymer control elasticity and flow properties
- To develop useful materials, we must understand how particles affect dynamics of polymers and vice versa



Maity, Bochinski, Clarke et al. *Nanoscale* (2014).



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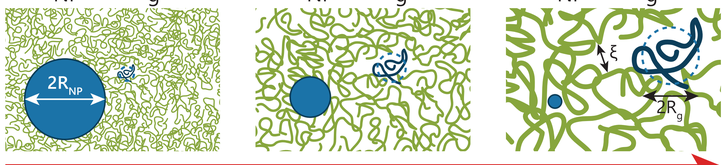
Particle Dynamics in Polymer Solutions

Particle dynamics depend on bulk viscoelasticity	Particle dynamics couple to polymer relaxations	Particle dynamics depend on solvent and void geometry
$R_{NP} > R_g, \xi$	$R_{NP} \approx R_g, \xi$	$R_{NP} < R_g, \xi$



Decreasing particle radius

- When particle is similarly sized to polymer, dynamics qualitatively and quantitatively deviate from Stokes-Einstein predictions [2,3]
- At short times, particle locally trapped by polymer and moves subdiffusively
- At long times, particle motion becomes diffusive but faster than expected
- Particle dynamics couple to polymer dynamics so that long-time diffusivity scales as $D \sim (R_{NP}/\xi)^{-2}$ [4,5]
- **Do interparticle interactions affect particle dynamics in presence of polymer?**

References

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[5] R. Poling-Skutvik, R. Krishnamoorti, and J. C. Conrad, *ACS Macro Lett.* **4**, 1169 (2015).
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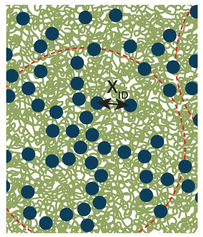
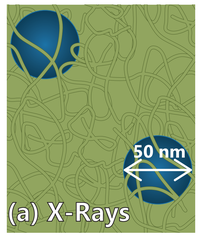
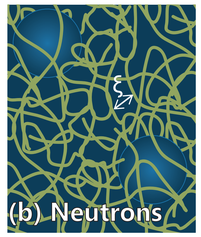
[7] P. G. De Gennes, *Physica* **25**, 825 (1959).

Experimental Materials and Methods

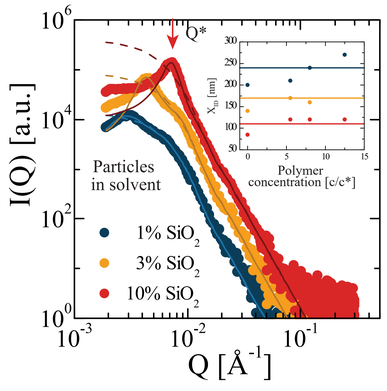
- Charged silica nanoparticles dispersed in solutions of polystyrene dissolved in 2-butanone
- Scattering techniques isolate structure and dynamics of individual components
  - (a) X-ray contrast increases with atomic number and measures particle structure and dynamics
  - (b) Neutron contrast related to concentration of hydrogen and deuterium and measures polymer properties





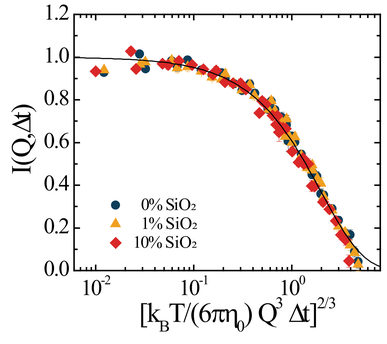


Particles Well-Dispersed and Interacting



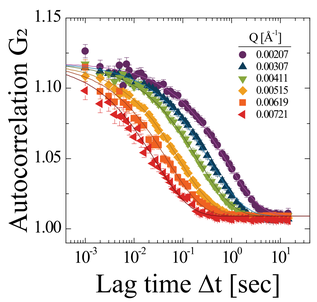
- Small angle x-ray scattering measures particle structure
- Charged particles repel each other and leads to free energy minimum at interparticle spacing X_{ID}
- Energy minimum results in peak in I(Q) at $Q^*=2\pi/X_{ID}$
- X_{ID} ranges from 100 nm to 250 nm depending on particle concentration

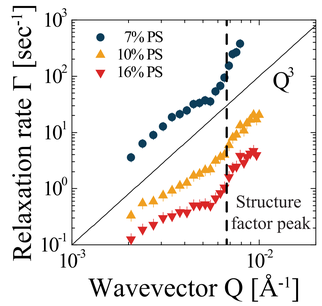
Polymer Relaxations Unaffected



- Neutron spin echo spectroscopy measures dynamics of polymer
- Polymer relaxes according to Zimm model [6]
- Relaxations controlled by hydrodynamics and unperturbed by particles
- Particle-polymer coupling unaffected in presence of interacting particles

Subdiffusive Particle Dynamics





- X-ray autocorrelation curves G_2 fit to stretched exponentials

$$G_2 = A + B \exp(-2(\Gamma\Delta t)^{\alpha})$$

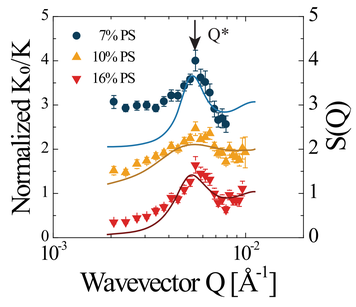
- Relaxation rates Γ scale as wavevector Q^3, consistent with subdiffusive dynamics
- Subdiffusive dynamics arise from coupling to polymer relaxations [4,5]
- Relaxation rates decrease with increasing polymer concentration due to increase n viscosity
- Local deviations from Q^3 scaling occur at Q*

Particle Structure Slows Dynamics

- De Gennes showed that structure and dynamics are inversely related in diffusive systems [7]

$$D(Q) \sim 1/S(Q)$$

- Energy minimum that results in peak in S(Q) slows relaxations over Q*
- Extend to subdiffusive systems by defining $K = \Gamma/Q^3$, analogous to diffusivity
- Relaxations out of energy minimum are slowed



Conclusions

- Polymer relaxes according to Zimm model and unperturbed by particles because of neutral interactions
- Particle dynamics are subdiffusive as they couple to polymer relaxations
- Particle interactions result in an energy minimum, slowing relaxations over Q* even with subdiffusive dynamics
- To understand bulk relaxation properties, must consider both particle-polymer and particle-particle interactions

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