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Dynamics of Particles in Soft Matter¹

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Can the properties of materials be deduced from the analysis of the trajectories of probe particles diffusing through them? The anomalous diffusion of a particle in complex media could be due to three fundamental reasons: (1) Viscoelastic response of the medium to the deformation imposed on it by the moving particle; (2) The particle could be attracted to some regions of heterogeneous medium and be temporarily localized in these “sticky” regions; (3) The particle is repelled from some regions of the medium and has to go over different energy barriers in order to diffuse through this medium. Can one determine which of these fundamental reasons cause the anomalous diffusion? We propose a method of analyzing particle trajectories to answer this question and to determine the corresponding properties of complex media such as distribution of relaxation times or energy distribution of attractive regions. We use scaling theory to derive the time dependence of the mean-square displacement $\langle r^2(t) \rangle$ of a probe nanoparticle in polymer solutions and melts. We distinguish several qualitatively different cases depending on the size d of the particle in comparison to solution correlation length ξ and tube diameter a for entangled polymer liquids. We also describe a hopping mechanism for diffusion of particles larger than mesh size of polymer solids (networks and gels). We solve activated hopping model in which particle experiences thermally activated jumps between neighboring wells of different energy depths. We find that the particle diffusion is ordinary Brownian (not anomalous) if the width of the distribution of well energies ΔU is smaller than thermal energy kT . In the opposite case ($\Delta U > kT$) we discover the surprising result that although jumps between neighboring wells are completely random and uncorrelated, the particle displacements during consecutive time intervals are correlated. The source of these correlations is that the particle can be located in the same well during both time periods. As the result, while the mean square displacement of the particle is still Brownian, the distribution of displacements is non-Gaussian and is almost exponential.

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