Theory of Percolation in Fluids of Long Molecules

Kevin Leung\textsuperscript{1} and David Chandler\textsuperscript{1}

Received February 14, 1991

We use the reference interaction site model (RISM) integral equation theory to study the percolation behavior of fluids composed of long molecules. We examine the roles of hard core size and of length-to-width ratio on the percolation threshold. The critical density $\rho_c$ is a nonmonotonic function of these parameters exhibiting competition of different effects. Comparisons with Monte Carlo calculations of others are reasonably good. For critical exponents, the theory yields $\gamma = 2\nu = 2$ for molecules of any noninfinite length $L$. When $L$ is very large, the theory yields $\rho_c \sim L^{-2}$. These predictions compare favorably with observations of the conductivity for random assemblies of conductive fibers. The threshold region where asymptotic scaling holds requires the correlation length $\xi \sim (\delta\rho/\rho_c)^{-\nu}$ to be much larger than $L$. Evidently, the range of densities in this region diminishes as $L$ increases, requiring that density deviations from $\rho_c$ be no larger than $\delta\rho \sim L^{-2}$. Otherwise, crossover behavior will be observed.

KEY WORDS: Percolation; RISM integral equation.

1. INTRODUCTION

Many phenomena which occur in disordered systems can be understood in terms of the connectivity and clustering of particles. Higher densities increase the tendency of particles to cluster together. At the critical percolation density $\rho_c$, which is in general dependent upon temperature and microscopic details, a macroscopic cluster appears, spanning the entire system. This sharp geometric phase transition is the percolation transition (see, e.g., ref. 1). It is often accompanied by drastic changes in the physical properties of the system. The sol–gel transition and the insulator–conductor transition in composite materials can be two such examples. For fluid
systems, the effects of anisotropy, intermolecular correlations, and density fluctuations seem best described by continuous percolation rather than by lattice models. In this paper we apply a version of the reference interaction site method (RISM) to examine the roles of molecular shape and excluded volume on the percolation transitions in fluids.

The Ornstein-Zernike integral equation approach to continuum percolation and its solution within the Percus-Yevick approximation were introduced by Coniglio et al. Chiew and Glandt applied this method to calculate among other things the critical densities of permeable-sphere models. Chiew and Stell improved upon this approximation with a type of generalized mean spherical approximation. Stratt and co-workers seem to have been the first to implement these types of integral equations with proper account for excluded volume, and they predicted trends that are in qualitative agreement with Monte Carlo calculations. Lupkowski and Monson and Laria and Vericat extended this approach to treat fluids composed of nonspherical particles by employing the interaction site formalism of Chandler and co-workers (see refs 14 for reviews). Our work described herein rests upon the contributions of Lupkowski and Monson and of Laria and Vericat. Excluded-volume effects, which generally dominate the intermolecular structure of liquids, were not directly taken into account by these workers. Nor did they consider extremely long molecules. Others have considered percolation with very long molecules (see, e.g., refs. 16), but often employed approximations that can be improved upon with the RISM approach. The present paper will address both the effects of excluded volume and long molecular lengths.

Further extensions to study the role of attractive particle–particle interactions or the presence of more than one species are clearly feasible. Such extension have been carried out, for example, by Xu and Stell and by Chiew et al., respectively, for spheres, but these apparent extensions are not the focus of this paper.

The remainder of this paper is organized as follows. In Section 2 we review the pertinent interaction-site equations and specify the model we are using. The molecular size and shape dependence of $\rho_c$ and the critical behavior near percolation determined from numerical solutions of RISM integral equations are examined in Section 3. The paper is concluded in Section 4 with a discussion containing analytical analysis and proposals for future work. An Appendix provides some details pertaining to our calculations that are omitted from the main text.

\(^2\) Refs. 2–7 are representative but not inclusive of the large literature in this area.