

## Conductivity from simulations of percolating systems of interacting particles

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1987 J. Phys. A: Math. Gen. 20 3029

(<http://iopscience.iop.org/0305-4470/20/10/044>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 31/05/2010 at 19:42

Please note that [terms and conditions apply](#).

## Conductivity from simulations of percolating systems of interacting particles

N A Seaton and E D Glandt

Department of Chemical Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA

Received 27 August 1986, in final form 7 October 1986

**Abstract.** The electrical conductivity of an equilibrium system of particles interacting according to a surface adhesion potential was studied by means of Monte Carlo simulations. Results for the conductivity in the region of the percolation threshold are reported as a function of particle volume fraction and temperature. The conductivity exponent  $\mu$  was found to be  $1.6 \pm 0.2$ , in agreement with experimental measurements on microemulsions but significantly different from the reported lattice value of about 2.0.

The electrical conductivity of a two-phase medium in which one phase is conducting and the other insulating is strongly dependent on the structure of the medium. If the conducting phase consists of particles dispersed in a continuous insulating phase, conduction only occurs above the percolation threshold for the dispersed phase. A possible example of such a system is a water-in-oil microemulsion (van Dijk 1985). In this case, the oil phase is almost entirely non-conducting and the small conductivity that is observed below the percolation point is primarily due to the migration of charged droplets. If the attractive forces between the droplets are sufficiently strong, the system will percolate at some droplet concentration and the conductivity will increase by several orders of magnitude (Cazabat *et al* 1980). The considerable influence exerted by the interparticle forces on the percolation threshold in equilibrium microemulsions has been illustrated experimentally by Cazabat, Langevin and co-workers (Cazabat *et al* 1980, 1982, 1984, Cazabat and Langevin 1981). Although several workers have reported simulation results for the conductivity of model systems in which conducting and insulating elements are constrained to lattice sites and for non-interacting continuum models, it seems that no results have been reported for continuum models of interacting particles. Lattice models have enjoyed substantial success in the study of the critical behaviour in the vicinity of the percolation threshold, but they do not necessarily capture the true fluid nature of equilibrium percolating systems. Notably, the value of the critical exponent for conduction,  $\mu$ , which is reported for three-dimensional lattice models is different from that measured experimentally in microemulsions. The conductivity,  $\sigma$ , near the percolation threshold is found experimentally to be governed by the scaling law

$$\sigma \propto (\eta - \eta_p)^\mu. \quad (1)$$

Here,  $\eta = \pi r d^3 / 6$  is the particle volume fraction, where  $\rho$  is the number density of particles and  $d$  is the particle diameter. Recent estimates of  $\mu$  for three-dimensional lattices are in the range 1.87-2.0 (Derrida *et al* 1983, Pandey and Stauffer 1983, Sahimi

*et al* 1983). Jerauld *et al* (1984) found the similar value of 2.02 for a Voronoi tessellation, a continuum model in which the nodes are randomly distributed in space. On the other hand,  $\mu$  has been measured as  $1.55 \pm 0.1$  and  $1.6 \pm 0.1$  for electrical conductivity in two different microemulsions by Lagues (1979) and as  $1.68 \pm 0.05$  by Bhattacharya *et al* (1985). These measured values are consistent with each other and significantly less than the values obtained using lattice models or the Voronoi tessellation.

In this paper we report a Monte Carlo investigation of the conductivity of an equilibrium dispersion of conducting particles in an insulating medium. The particles interact according to the adhesive-sphere potential, which is one of the simplest models to incorporate an attractive interaction, the limiting form of the square-well potential as the well becomes infinitely deep but only infinitesimally wide. The adhesive potential is given by

$$\begin{aligned} \exp(-\beta u(r)) &= \frac{d}{12\tau} \delta(r-d) & r \leq d \\ &= 1 & r > d \end{aligned} \quad (2)$$

where  $\beta = (kT)^{-1}$ ,  $k$  is Boltzmann's constant and  $\delta$  is the Dirac delta. The attractive well has the nature of an 'adhesion' on the surface of a spherical particle of diameter  $d$ .  $\tau$  is a dimensionless indicator of the temperature;  $\tau^{-1}$  represents the adhesiveness of the particles. Because the divergence of the Boltzmann factor occurs simultaneously with the vanishing of its width (or degeneracy), the probability that one particle finds itself in the potential well of another is finite. The Monte Carlo simulation method (Seaton and Glandt 1986, 1987b) for adhesive spheres and the aggregation and percolation behaviour of the adhesive sphere fluid (Seaton and Glandt 1987a) have been presented in separate publications and will not be discussed here.

If the ratio of the dispersed (particulate) phase conductivity to that of the continuous phase,  $\alpha$ , is sufficiently large, all the current flows within the particulate phase and between pairs of particles which are very close together. Each particle can then be considered to be a node in a resistor network and the calculation of the conductivity of a configuration generated in the course of the simulation is reduced to the solution of Kirchhoff's current law at each node (Kirkpatrick 1973)

$$\sum_{ij} g_{ij} (V_i - V_j) = 0 \quad (3)$$

where  $g_{ij}$  is the conductance across the gap between particles  $i$  and  $j$ , and  $V_i$  and  $V_j$  are the potentials of particles  $i$  and  $j$ , respectively. The calculation of the effective conductivity now amounts to the solution of a system of linear algebraic equations.

We have calculated the effective conductivity in a system of adhesive spheres in the limit as  $\alpha \rightarrow \infty$ . In this limit, conduction occurs only between particles at contact. Batchelor and O'Brien (1977) have obtained analytical results for the resistance,  $R$ , between two spheres at or near contact and shown that it is well defined in the above limit

$$R = [2\pi d\sigma_c \ln(\alpha^2)]^{-1} \quad (4)$$

where  $\sigma_c$  is the conductivity of the continuous phase. Because in the model potential considered here interacting particles are in direct contact, the interparticle resistance is a constant for all touching pairs, and is zero for pairs which are not touching. In an experimental system, on the other hand, neighbouring particles would adopt a range of separations causing the interparticle resistance to vary. As the interparticle potentials

in real systems are in general poorly known, it might in any case be difficult to produce by simulation a realistic distribution of interparticle resistances.

The conductivity which is reported here is that of a very large cubic system composed of replicas of the small system which is being simulated. (This is equivalent to the application of periodic boundary conditions.) A potential gradient is notionally applied to the infinite system. A constant potential difference therefore exists between any particle in the small system and its image in an adjacent replica system which has a different coordinate in the direction of the applied gradient. As the set of Kirchhoff's law equations is solved only for the small system itself, this must be taken into account in the boundary conditions for the conduction problem. In the direction of the potential gradient, therefore, the appropriate boundary condition is that the potential of a particle at the edge of a neighbouring replica differs from that of the corresponding particle in the small system by  $\pm\Delta V$ , while in the other cartesian directions they are at the same potential as the corresponding particle in the small system. The boundary condition in the direction of the gradient differs from the one usually employed, i.e. the application of a potential difference directly across the small system without considering periodic boundary conditions in this direction. The boundary conditions used here should be expected to yield conductivities closer to those of true macroscopic systems. The Kirchhoff's law equations were solved only for configurations which had already been determined to be percolating in the direction of the applied gradient, as the conductivity of other configurations is zero.

Most of the simulations were carried out with systems of 108 particles. Some simulations were carried out with systems of 32 particles to determine the effect of system size on the measured conductivity. The difference in conductivity between the two systems was slight, being within the experimental uncertainty except for densities very close to the percolation threshold,  $\eta_p$ , when the absolute difference was nevertheless small. For this reason, the 108-particle system was considered to accurately represent the macroscopic system, except very close to the percolation threshold. Some 256-particle runs were carried out at the percolation threshold. Because the structure of the percolating cluster changed rather slowly, the conductivity was calculated only every  $10N$  Monte Carlo steps, where  $N$  is the number of particles in the system. The number of configurations examined was between 1000 and 6750 for  $N = 108$  and between 1100 and 1760 for  $N = 256$ .

Figure 1 shows the reduced conductivity of suspensions of adhesive spheres at two temperatures,  $\tau = 0.10$  and  $\tau = 0.13$ , as the density varies. The percolation thresholds, which were determined independently of the conductivity calculations (Seaton 1986), are  $\eta_p = 0.123 \pm 0.003$  at  $\tau = 0.1$ , and  $\eta_p = 0.154 \pm 0.003$  at  $\tau = 0.13$ . The appropriate reduced conductivity is  $\sigma R d$ , where  $R$  is the interparticle resistance, as before. Although the dependence of the conductivity on the thermodynamic state is complex, being strictly an  $N$ -particle cooperative property, it must be an increasing function of the average coordination number. Considering that the coordination number increases with increasing density and decreasing temperature, this effect is indeed evident in figure 1. Because it does not represent the behaviour of a macroscopic system, the conductivity below the percolation threshold is not shown in figure 1, although because of the finite-size effect it is actually measured to be non-zero below  $\eta_p$ .

Clearly, the onset of percolation and the increase in conductivity above the percolation threshold are the results of the same microscopic phenomenon, i.e. increasing connectedness. It makes sense, therefore, to ask to what extent the conductivity is correlated with the percolation threshold. Figure 2 shows the data of figure 1 but with

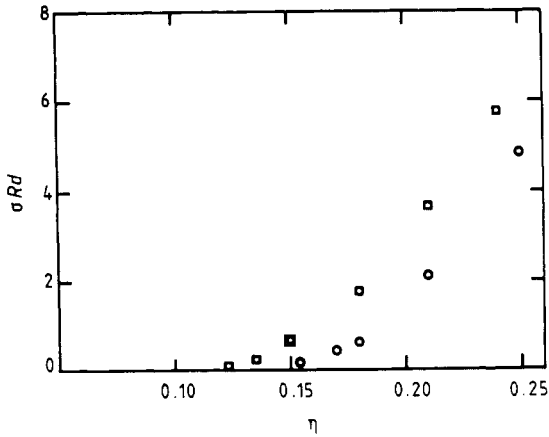


Figure 1. Reduced conductivity plotted against  $\eta$  for  $\tau = 0.1$  (squares) and  $\tau = 0.13$  (circles).

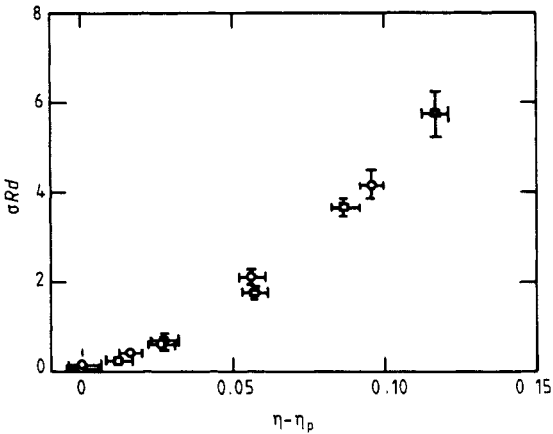


Figure 2. Reduced conductivity plotted against  $(\eta - \eta_p)$  for  $\tau = 0.1$  (squares) and  $\tau = 0.13$  (circles).

the curves shifted so that the abscissa is  $\eta - \eta_p$ , rather than  $\eta$ . To within the statistical uncertainty, the data collapse to a single curve. The error bars in  $\eta$  are due to the estimated uncertainty in  $\eta_p$ , given above; for any  $\tau$ , the error must of course be in the same sense for all data points. This suggests that, to a good approximation, the reduced conductivity may depend only on the difference between the particle volume fraction and the percolation threshold.

In this work, finite-size scaling was employed to calculate  $\mu$  from the adhesive-sphere simulation data. The finite-size scaling equation is (Mitescu *et al* 1982)

$$\sigma \propto L^{-\mu/\nu} \quad (5)$$

where  $L$  is the size of the system and  $\nu$  is the universal correlation length exponent (0.88 in three dimensions).  $\mu$  was obtained from a plot of  $\ln \sigma$  against  $\ln L$  for systems of 32, 108 and 256 particles for  $\tau = 0.1$  (figure 3) and 0.13. Despite the rather small size of the smallest system, the scaling plots were quite linear.

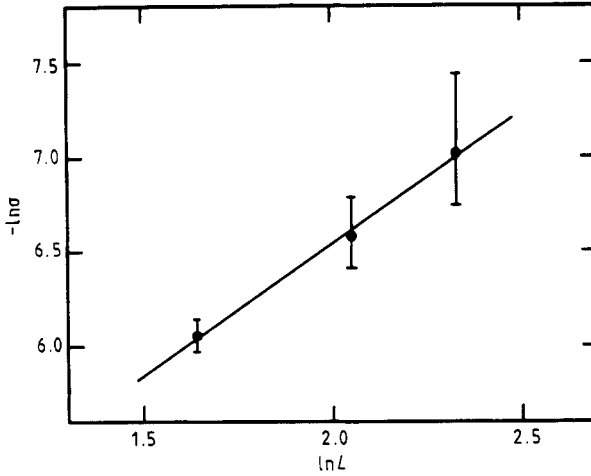


Figure 3. Finite-size scaling plot for  $\tau = 0.1$ .

Taking into account the experimental uncertainty,  $\mu$  was determined to be between 0.75 and 1.78 for the  $\tau = 0.1$  data, and between 1.45 and 1.80 for the  $\tau = 0.13$  data. Assuming that the scaling law holds for systems of this size, the best estimate of the conduction exponent is  $\mu = 1.6 \pm 0.2$ . These simulations were carried out on systems considerably smaller than are often used with lattice models, the reason being that continuum Monte Carlo simulations with interacting particles are considerably more time consuming. This is especially true in the case of adhesive particles, because of the difficulty in generating configurations where the particles are attached to one another (Seaton and Glandt 1986, 1987b). A simulation near the percolation threshold for a system of  $N = 256$  particles required about 3 h of CPU time on a Cray XMP. The simulation of larger systems was therefore deemed impractical. There would thus be the possibility of a systematic error in the estimation of  $\mu$  if the systems we have studied were not in the scaling region, although the linearity of the scaling plots and the corresponding plots for the percolation threshold suggest that finite-size scaling holds well for systems of these sizes. Because of the limited availability of computer time, finite-size scaling was applied only at the best estimate of  $\eta_p$  for each  $\tau$ ; the error in  $\eta_p$  was not taken into account and the estimated error in  $\mu$  is due only to the error in the conductivity calculations. The value of  $\mu$  obtained from the simulations is significantly different from the values measured using lattice models and is in good agreement with the values measured experimentally in microemulsions (1.5)–(1.7). Several workers (Kogut and Straley 1979, Ben-Mizrahi and Bergman 1981, Halperin *et al* 1985, Sen *et al* 1985) have shown for non-interacting systems that, if the values of the resistances vary from resistor to resistor (being chosen at random from a probability distribution), the exponent governing the conductivity may be greater than the exponent found for lattice-based models in which the resistances are all the same. Because it appears that  $\mu$  is always increased by the introduction of a distribution of resistances, this effect cannot account for the difference between the experimental microemulsion value and the generally accepted lattice value.

In appears that this is the first time that the non-lattice value has been observed in a model system where the interparticle resistance is fixed. Our result supports the evidence of measurements on microemulsions that equilibrium continuum systems are

in a different universality class from lattice systems, from the point of view of their transport properties.

## References

- Batchelor G K and O'Brien R W 1977 *Proc. R. Soc. A* **355** 313  
Baxter R J 1968 *J. Chem. Phys.* **49** 2770  
Ben-Mizrahi A and Bergman D J 1981 *J. Phys. C: Solid State Phys.* **14** 909  
Bhattacharya A, Stokes J P, Kim M W and Huang J S 1985 *Phys. Rev. Lett.* **55** 1884  
Cazabat A M, Chateney D, Geuring P, Langevin D, Meunier J and Sorba O 1984 *Surfactants in Solution* ed K L Mittal and B Lindeman (New York: Plenum) p 1737  
Cazabat A M, Chateney D, Langevin D and Meunier J 1982 *Faraday Disc. Chem. Soc.* **76** 291  
Cazabat A M, Chateney D, Langevin D and Pouchelon A 1980 *J. Physique Lett.* **41** L441  
Cazabat A M and Langevin D 1981 *J. Chem. Phys.* **74** 3148  
Derrida B, Stauffer D, Herrmann H J and Vannimenus J 1983 *J. Physique Lett.* **44** L701  
Halperin B I, Feng S and Sen P N 1985 *Phys. Rev. Lett.* **54** 2391  
Jerauld G R, Scriven L E and Davis H T 1984 *J. Phys. C: Solid State Phys.* **17** 3429  
Kirkpatrick S 1973 *Rev. Mod. Phys.* **45** 574  
Kogut P M and Straley J P 1979 *J. Phys. C: Solid State Phys.* **12** 2151  
Lagues M 1979 *J. Physique Lett.* **40** L331  
Mitescu C D, Allain M, Guyon E and Clerc J P 1982 *J. Phys. A: Math. Gen.* **15** 2523  
Pandey R B and Szauffer D 1983 *Phys. Rev. Lett.* **51** 527  
Sahimi M, Hughes B D, Scriven L E and Davis H T 1983 *J. Phys. C: Solid State Phys.* **16** L521  
Seaton N A and Glandt E D 1986a *J. Chem. Phys.* **84** 4595  
— 1987a *J. Chem. Phys.* in press  
— 1987b submitted  
Seaton N A 1986 *Dissertation, The Structure, Percolation and Transport Properties of Particulate Dispersions* University of Pennsylvania  
Sen P N, Roberts J N and Halperin B I 1985 *Phys. Rev. B* **32** 3306  
van Dijk M A 1985 *Phys. Rev. Lett.* **55** 1002