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13. ABSTRACT (Maximum 200 words)

This report outlines progress during the grant period on non-steady fluid flow processes in porous networks, the structure of growing networks, and the applications of statistical mechanics to fundamental non-equilibrium processes. In flow processes a statistical theory for the clogging time of a filter was constructed that successfully accounts for numerical simulations of filtration in porous networks. In related research, a comprehensive theory was developed for the infiltration and breakthrough of a contaminant as it passes through a neutralizer-impregnated porous medium. Finally, a detailed theory was constructed for the dissolution kinetics of a solid medium under action of a reactive acidic fluid whose motion is strongly biased.

In an independent area, fundamental theoretical advances about the structure of growing networks was made by applying the rate equations approach. By this formalism, the degree distributions of growing networks, as well as a host of basic geometrical properties were quantified. Finally, new results were obtained about the kinetics of a variety of fundamental non-equilibrium processes, such as the kinetics of traffic clustering, aggregation, annihilation, and fragmentation.

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1. Foreword

During the period of this grant, we made significant progress in several important areas. First we constructed a statistical theory for the clogging time of a filter that is based on a simplified model for the motion of contaminant particles through the medium, together with basic facts from extreme value statistics. This theory accounts for numerical simulations of filtration in porous networks. Various features of filtration that are related to this theoretical research have been under experimental investigation by Army Research personnel at the Natick ERDC.

In a related research topic, we developed a comprehensive theory for the infiltration and breakthrough of a contaminant that is passing through a porous medium in which the walls of the pore space are coated with a neutralizing material. We also constructed a detailed theory for the dissolution kinetics of a solid medium under the action of a reactive acidic fluid where the motion of the dissolving molecules is anisotropic.

In a very different area, we made fundamental theoretical advances about the structure of growing networks. By applying the rate equations approach for determining the underlying distributions of non-equilibrium systems, we are able to quantify the degree distributions of growing networks, as well as a host of basic geometrical properties. Some of these predictions help to provide a quantitative description of the world-wide web.

Finally, we have continued research on the applications of statistical mechanics to a variety of fundamental non-equilibrium processes, such as the kinetics of traffic clustering, aggregation, annihilation, and fragmentation. Details on these projects are provided below.

2. Filtration: Clogging Time and its Distribution

We developed an extremal theory for the mean clogging time of a filter, as well as the distribution of clogging times. In our theory, we describe the exact particle trajectories by a simplified picture in which each particle attempts to block the largest available pore along its trajectory. Our predictions were tested by numerical simulations that relied on a simple but powerful computational method to simulate the simultaneous motion and trapping of many particles.

Our theory applies to the situation where typical pore sizes are of the order of particle sizes or smaller. A basic element of our theory is that pores tend to get blocked in size order. This arises because particles are more likely to enter larger pores, since the entrance rate into a pore is proportional to the local flux entering that pore. Based on this observation, we considered the extreme limit where each particle always enters the largest available pore at each junction. This theoretical construction drastically simplifies the description to the point that we are able to compute the mean clogging time and its distribution.

Another simplifying feature is based on the fact that clogging preferentially occurs upstream in the network. Thus it is sufficient to consider short systems, the most extreme of which is a single parallel array of tubes. Since tubes are blocked in size order according to our modelling, we can determine the permeability of the array when $k^{\rm th}$ smallest tube is blocked from basic statistical ideas. The ratio of this partial permeability to the initial permeability determines a corresponding scale for the time until this event occurs. Finally, given the pore-size distribution, we use extreme value statistics to obtain the size distribution of the smallest pore in the sample. Due to the one-to-one connection between the size of the pore and the time scale at which it is blocked, we can recast the size distribution of the smallest pore into the distribution of times at which this smallest pore is blocked.

By this approach we found that the distribution of clogging times $P(t)$ has a simple functional form with a power-law long-time tail,

$$P(t) \sim \frac{\tau^{\nu-1}}{t^\nu}\, e^{-(\tau/t)^{\nu-1}}.$$

Here τ is the most probable value of the clogging time, and the exponent ν depends on details of the particle size distribution, but for physical situations is typically between 5/4 and 3/2. This theoretical description is in excellent agreement with our simulations of filtration on large square lattice tube networks.

3. Infiltration Kinetics

We studied the kinetics of infiltration processes in which dynamically-neutral contaminant particles ("invader"), which are suspended in a flowing carrier fluid, penetrate a porous medium. The progress of the invader particles is impeded by their trapping on active "defender" sites on the surfaces of the medium. As defenders are used up, the invader penetrates further and ultimately breaks through the system. We studied this process in the regime where the particles are much smaller than the pores, so that the permeability change due to trapping is negligible. We developed a series of discrete network models of increasing realism to describe the basic characteristics of infiltration. We showed that a simple quasi-one-dimensional model appears to capture many of the quantitative features that we observed in numerical simulations of infiltration on lattice models of porous networks.

With this approach, we determined basic dynamical properties of infiltration, including the propagation velocity of the invasion front, as well as the shapes of the density profiles of the invader and defender particles. The predictions of our model agree qualitatively with a variety of experimental results on the breakthrough times during infiltration, as well as the time dependence of the invader concentration at the output. Our results also provide practical guidelines for improving the design of deep bed filters in which infiltration is the primary separation mechanism.

4. Dissolution Kinetics

We investigated the kinetics of solid dissolution due to the injection of a steady stream of reactive particles at a single point. The new feature of our work is that we considered the situation in which a global bias exists, in addition to the diffusive motion of the reactive particles. The bias may be provided by an electric field acting on reactive ions or a gravitational field acting on a flowing fluid. We find that the bias is a relevant perturbation with respect to diffusion and leads to a different dissolution process from that caused by isotropic diffusion. As a function of time, the dissolved region is strongly anisotropic, with its length growing in time as $\xi_\parallel \sim t^{2/(d+1)}$, while the transverse width grows as $\xi_\perp \sim t^{1/(d+1)}$, where d is the spatial dimension of the system. Within the dissolved cavity, the concentration of reactive particles follows the steady state profile of biased diffusion. This corresponds to the solution of the anisotropic Laplace equation. From this solution, we found that the total number of reactive particles within the cavity grows as $t^{2/(d+1)}$. We also found intriguing dimension-dependent behavior for the spatial distribution of the reactive particles.

We also extended our investigation to the case of variable reaction rate (equivalently, weak acid strength). In the limit of weak acid, the dissolution boundary becomes smoother and grows more slowly, since many more reactive particles particles must impinge on the surface to dissolve a unit volume of the substrate material. We found that the effect of varying acid strength is equivalent, in a scaling sense, to a time rescaling. behavior.

5. Structure of Growing Networks

The structure of growing random networks was investigated by a simple rate equation approach. These networks are built by adding nodes successively and linking each to an earlier node of degree k with an attachment probability A_k. Such growth processes mimic what occurs in building the hyper-link graph that underlies the world-wide web.

When A_k grows slower than linearly with k, the number of nodes with k links, $N_k(t)$, decays faster than a power law in k, while for A_k growing faster than linearly in k, a single node emerges which connects to nearly all other nodes. When A_k is asymptotically linear, $N_k(t) \sim tk^{-\nu}$, with ν dependent on details of the attachment probability, but in the range $2 < \nu < \infty$. We also determined the size distributions of the in-components and out-components of the network with respect to a given node – namely, its "descendants" and "ancestors".

We extended the model to account for the common situation where there are different in-degrees and out-degrees at each node. The in-degree is the number of incoming links to a given node (and *vice versa* for out-degree). To construct networks with this property, the network is built by (i) creation of new nodes which each immediately attach to a pre-existing node, and (ii) creation of new links between pre-existing nodes. This process naturally generates correlated in- and out-degree distributions. When the node and link creation rates are linear functions of node degree, these distributions exhibit *distinct* power-law forms. By tuning the parameters in these rates to reasonable values, exponents which agree with those of the world-wide web were obtained.

Finally, we adapted the rate equation approach more detailed structural information about growing networks. This includes the joint order-degree distribution, the degree correlations of neighboring nodes, as well as simple global properties. Our theory provides the most comprehensive description of the geometric features of growing networks that is currently available.

6. Cooling of Inelastic Gases

We investigated the cooling of inelastic gases. The governing Boltzmann equation with uniform collision rates was solved analytically for the cases of spatially homogeneous gases, for gases with a dilute concentration of impurities, and for mixtures. Generally, the energy dissipation leads to velocity distributions with a relatively high population in the high-energy tails, and also the correlation of different velocity components. In the freely cooling case, the departure from the elastic behavior is especially profound – rather than being Gaussian, the velocity distribution develops an algebraic high-velocity tail, with an exponent that depends sensitively on the dimension and on the degree of dissipation.

Other characteristics also demonstrate unusual behaviors. For example, moments of the velocity distribution exhibit multiscaling, and the velocity autocorrelation function decays algebraically with time. In the forced case, where energy is injected into the system at a constant rate, the steady state velocity distribution decays exponentially at large velocities. An impurity immersed in a uniform inelastic gas may or may not mimic the behavior of the background gas, and the departure of properties of the impurity from that of the background is characterized by a series of phase transitions.

7. Phase Transitions in Traffic Flows with Passing

We investigated the traffic dynamics of a one-dimensional system of particles (cars) moving on a line. Cars either move freely with quenched intrinsic velocities, or belong to clusters that form behind slower cars. In each cluster, the next-to-leading car is allowed to pass and resume its free motion. Remarkably, the system undergoes a phase transition from a disordered phase for high passing rate, that is characterized by many passing events, to a jammed phase for low passing rate. In the disordered phase, the cluster size distribution decays exponentially in the large-size limit. In the jammed phase, the cluster-size distribution has a power-law tail and there is also an infinite-size cluster (that is, a cluster that contains a finite fraction of all the cars in the system). We solved the mean-field kinetic equations that account for the dynamics within the framework of the Maxwell approximation. These solutions correctly predict the existence of the phase transition and also account for the basic properties of the disordered phase. For the jammed phase, the Maxwell approximation also describes the formation of an infinite cluster and the power law tail of the size distribution of finite clusters.

8. Ballistic Annihilation Kinetics

By analytical solutions of the Boltzmann equation in conjunction with a scaling approach, we determined the kinetics of ballistic annihilation, namely the reaction $A+A \to 0$, in which each particle moves at a constant, but distinct velocity until a collision occurs. For the particular case of continuous initial particle velocity distributions, the particle density and the rms velocity decay with time as $c \sim t^{-\alpha}$ and $\bar{v} \sim t^{-\beta}$, respectively, with the exponents dependent on the initial velocity distribution and on the spatial dimension d. For example, in one dimension and for a uniform initial velocity distribution, $\beta = 0.23047\ldots$. In the opposite extreme of $d \to \infty$, the dynamics is universal and $\beta \to \left(1 - 2^{-1/2}\right) d^{-1}$. Although the Boltzmann equation framework is not exact, we believe that the exponent predictions are exact. Further, in the limit $d \to \infty$, the Boltzmann framework becomes exact and therefore the latter prediction is certainly correct.

9. Stochastic Aggregation

We investigated a class of stochastic aggregation processes that involve two types of clusters: active and passive. The character of a cluster is altered every time it undergoes aggregation, so that the coalescence of two active clusters may result in a passive cluster that does not participate in further aggregation. A concrete example is polymerization of linear polymers with end monomers being chemically active or inert.

The mass distribution for this system was obtained by analytical solution of the underlying rate equations for basic classes of aggregation rates. When the aggregation rate is constant, we found that the mass distribution of the passive clusters decays algebraically with mass in the large-mass limit. For aggregation rates that are proportional to the cluster masses, we found that the classical gelation phenomenon is suppressed when clusters can become inert. In this case, the tail of the mass distribution decays exponentially for large masses, and as a power law over an intermediate size range.

10. Travelling Wave Formulation of Fragmentation

We investigated a random bisection problem in which an initial interval of length x is cut into two random fragments at the first stage, then each of these two fragments is cut further, *etc.* We compute the probability $P_n(x)$ that at the n-th stage, each of the 2^n fragments is shorter than 1. Intriguingly, this fragmentation problem is a reformulation of the celebrated random binary search tree algorithm – the above number n can be identified with the height of the binary search tree. The fragmentation problem also corresponds to a directed polymer problem on a Cayley tree in which the cutting of an interval into two parts of relative lengths r and r' is represented by two bonds with "energies" $E = -\ln r$ and $E' = -\ln r'$ connecting a node (initial interval) with two daughter nodes. Then the statistics of the height can be re-expressed in terms of the statistics of the minimal energy of the directed polymer

We employed the techniques of travelling wave fronts to solve the polymer problem and then translate back these results to derive the exact asymptotic properties in the original search tree problem. Our method reproduces already known results for random binary trees, but the derivation is much simpler than in earlier work. More importantly, we obtained several new exact results. For example, we found a first leading correction to the average height, and we showed that the width of the height distribution is finite.

11. Recursive Fragmentation Processes

We investigated the evolution of the fragment size distribution in a class of recursive fragmentation processes. In the simplest such process, a newly formed fragment continues to participate in fragmentation with a fixed probability p, while with probability $1 - p$ it becomes stable and never fragments again. Such recursive fragmentation processes occur, for example, in DNA segmentation algorithms. Another example, is the fragmentation of a composite material, where small fragments of hard material may stop fragmenting because they are stronger than the composite itself.

We found that the size distribution approaches a stationary form that exhibits a power law divergence in the small-size limit. Furthermore, the entire range of acceptable values of decay exponent, consistent with mass conservation, can be realized in a specific process. We also showed that the recursive fragmentation process is non-self-averaging. This means that there are significant sample-to-sample fluctuations in the moments of the fragment size distribution. As a consequence, the fragment distribution in individual realizations of the fragmentation process can be quite different. We also determined basic characteristics of the extremes of the fragment size distribution.

Technology Transfer

I had substantive scientific interactions with Drs. Don Rivin, Heidi Schreuder-Gibson, and Phil Gibson of the Natick Army Research Laboratories. An experimental study of the kinetics of filtration, which was motivated in part by my theoretical research, is continuing. I provided theoretical support for this effort.

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1. “Stochastic Aggregation: Rate Equations Approach”, P. L. Krapivsky and E. Ben-Naim, *J. Phys. A* **33**, 5465 (2000).
2. “Stochastic Aggregation: Scaling Properties”, E. Ben-Naim and P. L. Krapivsky, *J. Phys. A* **33**, 5477 (2000).
3. “Particle Systems with Stochastic Passing”, I. Ispolatov and P. L. Krapivsky, Phys. Rev. E **61**, R2163 (2000);
4. “Clogging Time of a Filter”, S. Redner and S. Datta, *Phys. Rev. Lett.* **84**, 6018 (2000).
5. “Fragmentation with a Steady Source”, E. Ben-Naim and P. L. Krapivsky, *Phys. Lett. A* **275**, 48 (2000).
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7. “Extremal Paths on a Random Cayley Tree”, S. N. Majumdar and P. L. Krapivsky, *Phys. Rev. E* **62**, 7735 (2000).
8. “Traveling Waves, Front Selection, and Exact Nontrivial Exponents in a Random Fragmentation Problem”, P. L. Krapivsky and S. N. Majumdar, *Phys. Rev. Lett.* **85**, 5492 (2000).
9. “Multiscaling in Inelastic Collisions”, E. Ben-Naim and P. L. Krapivsky, Phys. Rev. E **61**, R5 (2000).
10. “Infiltration Through Porous Media”, W. Hwang and S. Redner, *Phys. Rev. E* **63**, 021508 (2001).
11. “Organization of Growing Random Networks”, P. L. Krapivsky and S. Redner, *Phys. Rev. E* **63**, 066123 (2001).
12. “Degree Distributions of Growing Networks”, P. L. Krapivsky, G. J. Rodgers, and S. Redner, *Phys. Rev. Lett.* **86**, 5401 (2001).
13. “Dissolution in a Field”, W. Hwang and S. Redner, *Phys. Rev. E* **64**, 041606 (2001).
14. “Ballistic Annihilation with Continuous Isotropic Initial Velocity Distribution”, P. L. Krapivsky and C. Sire, *Phys. Rev. Lett.* **86**, 2494 (2001).
15. “Nontrivial Velocity Distributions in Inelastic Gases”, P. L. Krapivsky and E. Ben-Naim, J. Phys. A. **35**, L147 (2001).
16. “Scaling, Multiscaling, and Nontrivial Exponents in Inelastic Collision Processes”, E. Ben-Naim and P. L. Krapivsky, Phys. Rev. E. **66**, 011309 (2002).
17. “Impurity in a Maxwellian Unforced Granular Fluid”, E. Ben-Naim and P. L. Krapivsky, Eur. Phys. J. E **8**, 507 (2002).
18. “Stable Distributions in Stochastic Fragmentation”, P. L. Krapivsky, I. Grosse, and E. Ben-Naim, to appear in Phys. Rev. E.

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1. Invited Talk, Workshop of Flexible Barriers, Natick Army Research Laboratories, April 15, 1999, Title: Filtration: Clogging and Dynamics.
2. Condensed-Matter Theory Seminar, Dartmouth University, Hanover, NH, May 27, 1999. Title: Gradient Clogging in Depth Filtration.
3. Invited Speaker, Workshop on Non-Equilibrium Dynamic Systems, University of Porto, Porto Portugal, June 6-11, 1999. Title: Kinetics of Clogging Processes.
4. Invited Speaker, Workshop on the Dynamics of Non-Equilibrium Systems, International Center for Theoretical Physics, Trieste, Italy, August 16-27, 1999. Title: Kinetics of Clogging Processes.
5. Departmental Colloquium, University of Virginia, Charlottesville VA, December 3, 1999. Title: Aggregation Kinetics in Gelation, Traffic, Wealth, and other Everyday Phenomena.
6. Departmental Colloquium, Brandeis University, Waltham, MA, September 19, 2000. Title: Aggregation Kinetics in Gelation, Traffic, Wealth, and other Everyday Phenomena.
7. Invited Talk, New England Complex Fluids Workshop, March 23, 2001. Title: How Does a Filter Clog?
8. Conference Presentation, TRI-Princeton Conference on Wetting and Nanocapillarity, June 25-27, 2001. Title: Clogging Time of a Filter.
9. Invited Talk, Army Research Office Workshop on Permselective Membranes, Aberdeen, Md., November 14-15, 2001. Title: Dynamics of Barrier Penetration.
10. Invited Talk, Materials Research Society Fall Meeting, Boston MA, November 2001. Title: How Long Does It Take For A Filter To Clog?
11. Invited Talk, International Conference on "Scaling and Phase Transitions in Complex Networks and Nonequilibrium Systems". Sponsored by the Asia Pacific Center for Theoretical Physics, Pohang, Korea, February 18-21, 2002. Title: Growing Networks.
12. Departmental Colloquium, Johns Hopkins University, Baltimore, Md., April 18, 2002. Title: The Statistical Mechanics of Popularity.
13. Invited Talk: Michigan Center for Theoretical Physics Conference on "Fronts, Fluctuations, and Growth", University of Michigan, Ann Arbor, MI, May 19-26, 2002. Title: Growing Networks.
14. Invited Talk, XVIII SITGES Conference "Statistical Mechanics of Complex Networks", Sitges, Spain, June 10-14, 2002. Title: Rate Equation Approach for Growing Networks.

Participating Scientific Personnel

Limei Xu, Graduate Student: 2000 - present.

Dr. Paul L. Krapivsky, Research Associate Professor: 1999 - present.