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i) Monte Carlo Calculation of Chemical Potential of a Stockmayer Fluid, J. Chem. Phys. (Accepted).

ii) Fractional Brownian Diffusion in Molecularly Thin Films, Science (To appear).

iii) On Spectral Measure and Monte Carlo Approaches to Flow in Heterogeneous Media, Water Resour. Res. (Accepted).

iv) Shear Melting of Molecularly-Thin Confined Films, Phys. Review B (Accepted).

v) Nonlocal Diffusion and Strain-Induced Liquification at Particulate Media, Applied Mechanics (In Press).

vi) Hierarchical Problems: Some conceptual Difficulties in the Development of Transport Equations, in Heat and Mass Transfer in Porous Media (ed) M. Quintard (In Press).

vii) Application of Multiple-Angle-of-Incidence Ellipsometry to the Study of Thin Films Adsorbed on Surfaces, Langmuir 7:2219-2229.

viii) On Adsorption and Diffusion at Rough Surfaces: A Comparison of Statistical Mechanic, Molecular Dynamics and Kinetic Theory, J. Chem. Phys. 95(8):6194-6195.

ix) Fluids in Micropores III: Self-Diffusion in a Slit-Pore with Hard Rough Walls, J. Chem. Phys. 95(7):5432-5436.

x) Nonlocal Transport Theories for Media with Microstructure, ASME, Applied Mechanics Div. 117, 17-22.

xi) Hierarchical Approaches to Transport in Heterogeneous Porous Media, Revs. Geophys. Supplement - U.S. National Report to International Union of Geodesy and Geophysics 1987-1990:263-269.

xii) On Diffusion in Fractal Porous Media, Water Resour. Res. 27(4):643-644.

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BRIEF OUTLINE OF RESEARCH FINDINGS AS DISPLAYED BY THE ABSTRACTS FROM THE ARTICLES CITED

Monte Carlo Calculation of Chemical Potential for the Stockmayer Fluid

The chemical potential of the Stockmayer fluid is computed by the canonical ensemble Monte Carlo methods of Widom, Bennett and Han. Both spherical cutoff and metallic Ewald sum techniques are employed. For the states studied it is found that the Ewald sum provides little improvement over the simpler spherical cutoff, that Bennett's and Han's methods produce essentially the same results, and that for certain states Widom's method is less accurate than Bennett's or Han's. The accuracy of the chemical potential calculated via the three methods was verified with Adams' version of the grand canonical ensemble Monte Carlo method.

Hierarchical Problems: Some Conceptual Difficulties in the Development of Transport Equations

An attempt is made to isolate several of the more significant conceptual difficulties encountered when developing transport theories via averaging. A number of somewhat esoterical formations are used as examples to motivate the discussion. The porous media are classified according to whether they possess discrete or continuous, and structural or functional hierarchy. Various methods are proposed to deal with the different categories of hierarchy.

Nonlocal Diffusion and Strain-Induced Liquification of Particulate Media

Previously the author has developed a nonlocal balance law for preasymptotic diffusion in media with microstructure and an approximate wavevector (k) and frequency dependent diffusion tensor which is valid for small $|k|$. The results have been applied to fractal media which induce a fractional Brownian trajectory. These concepts are viewed and discussed in the context of granular media. The author, in conjunction with co-workers at Purdue, has also conducted numerical experiments related to phase changes which are induced by strain in a Lennard-Jones fluid confined between infinite structured planes. These results are also reviewed and discussed in the context of granular flows.

Nonlocal Transport Theories in Media with Microstructure

Media that possess microstructure often have evolving heterogeneities. The canonical example of such a medium is a fractal porous formation. This type of medium has correlation functions with persistent tails, which suggests there is no well-defined discrete scale of motion. Consequently, nonlocal continuum or statistical theories must be applied to such systems. We discuss the application of a generalized Langevin theory in conjunction with irreversible thermodynamics to porous formations that have evolving heterogeneities. Specifically we derive nonlocal diffusion and dispersion equations and present closed expressions for the diffusion and dispersion tensors in the limit of small wavenumbers. Applications to fractal Brownian dynamics are discussed.

Hierarchical Approaches to Transport in Heterogeneous Porous Media

Most attempts to quantify heterogeneity have been based on the belief that a separation of scale exists between a highly heterogeneous "small" scale and a "large" scale which is homogeneous relative to the former. The major distinction between these two scales is that small scale variability is often irrelevant for the prediction of events on the large scale. While it is apparent that cases exist where there is a distinct dichotomy of scales, the more general (and frequent) case will be that heterogeneity exists at all scales. Hierarchical approaches to transport in porous media recognize the natural variability of geologic materials that serve as soils and aquifers. Recently, researchers have begun developing new theories and models of transport and transformation in heterogeneous porous media based on conceptual models of hierarchical spatial variability of geologic materials.

On Diffusion in Fractal Porous Media

Generalized hydrodynamics and irreversible thermodynamics are used to derive the relation between a general wave vector and frequency dependent diffusion tensor, and the power spectral density. The results are valid for porous media with evolving heterogeneities. An integrodifferential transport equation, valid in porous media with evolving heterogeneities, is presented.

Fluids in micropores. III. Self-diffusion in a slit-pore with rough hard walls

Self-diffusion coefficients for a model slit-pore consisting of Lennard-Jones (12,6) fluid constrained between two plane-parallel rough hard walls have been computed by standard microcanonical molecular dynamics. Fluid molecules collide impulsively with the walls, their speeds remaining unchanged, but the directions in which they rebound from the walls are chosen probabilistically so that the walls behave as Maxwell's "perfectly adsorbing" walls. For comparison, fluid contained in the same thermodynamic state by a pore with smooth walls has also been simulated. The local density profiles, which are the same in both rough and smooth-walled pores, show that the pore fluid forms distinct layers parallel with the walls. The rate of transverse diffusion (parallel with walls) within a given fluid layer depends markedly on its distance from the walls and on the nature of the walls. Transverse diffusion within the layer in contact with the rough wall is slower than that within the layer in contact with the smooth wall.

On Spectral Measure and Monte Carlo Approaches to Flow in Heterogeneous Media

A pedagogical approach to the spectral integral method as applied to flow problems is presented. The deterministic Fourier analog to the random spectral integral is highlighted, thus illustrating the close ties between the two. The general solution to the deterministic flow problem is used to illustrate that a weakly stationary conductivity field does not in general lead to a weakly stationary head field. Several alternative Monte Carlo methods are presented and compared to illustrate the problems associated with dropping terms of the form f'h' from the flow equation, where f and h are respectively perturbations in the conductivity and head fields.

Fractional Brownian Diffusion in Molecularly-Thin Films

Molecular relaxation in ultra-thin films has been studied by computer simulation of diffusion in a monolayer of atomic fluid constrained between two structured plane-parallel solid walls. The transverse alignment of the walls is varied to alter the microscopic environment in which the confined atoms move. Log-log plots of mean square displacement versus time yield straight lines of slope $d < 1$, where d depends on alignment and coordinate direction. That is the fluid envinces anisotropic fractional (fractal) Brownian motion. The fractal character is rationalized qualitatively in terms of the constrictive structure of the "tunnels" through which atoms must diffuse.

Shear Melting of Molecularly Thin Confined Films

Strain-induced melting of solid phases in a prototypal slit-pore (a rare gas constrained between two plane-parallel walls made up of rare-gas atoms fixed in the configuration of the (100) plane of the face-centered cubic lattice) is investigated by Monte Carlo calculations in the "isostress-isostrain" ensemble where the thermodynamic state of the pore phase is uniquely determined by fixed number of molecules, constant load or normal stress and constant temperature. If the walls are properly aligned laterally, a commensurate solid phase can form epitaxially. Moving the walls out of alignment creates a strained pore solid, which reacts (shear stress) by tending to realign the walls. If the shear strain is increased beyond a critical value, the pore solid begins to melt. However, melting is a continuous transition which does not immediately lead to a liquid, but rather a disordered phase that sustains a non-negligible shear stress. Shear melting is contrasted to ordinary melting at constant stress, which appears to be a first-order transition.

Application of Multiple-Angle-of-Incidence Ellipsometry to the Study of Thin Fluid Films Adsorbed on Surfaces

Many natural and technological processes are governed by the properties of thin films of water adsorbed onto mineral surfaces. The present study was undertaken to better understand the development of thin films. Previous ellipsometric measurements of water-film thickness on silicates at saturated vapor pressure have yielded thicknesses ranging from 10 to 1500 Å. However, these measurements relied on assumptions about the refractive indices of the film and substrate which were necessitated by the single-angle-of-incidence method used. The present study involved an environmental cell with flexible bellows as arms so that multiple-angle-of-incidence (MAI) measurements could be made. MAI measurements were interpreted with electromagnetic theory and resulted in the simultaneous measurement of the film thickness, refractive index, and extinction coefficient of the film and substrate. They were made on a fused silica surface after it was carefully cleaned and equilibrated with water vapor at seven relative vapor pressures (p/p° = 0.85, 0.90, 0.93, 0.95, 0.97, 0.98, and 0.995). The resulting film thicknesses (h) ranged from 24 to 90 Å, with only 3-4 Å surface roughness measured under vacuum, (p/p° = 0.0). Hysteresis between the desorption and adsorption branches was negligible. The refractive index of the water films in the range 24-50 Å agreed well with the bulk value of water, 1.332.

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