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13. ABSTRACT (Maximum 200 words) A fundamental understanding of the physical and chemical basis for frost heaving is of utmost importance for improving the design of structures for use in cold regions. The research reported here represents a multidisciplinary effort to develop a molecular-scale understanding of this cold region phenomena. Propagation of the molecular-scale information to a field scale is also important and the scale-up problem has also been addressed. A multiphase, multicomponent hybrid theory of mixtures approach was used to scale up information. Equilibrium and nonequilibrium statistical mechanical tools were developed and employed to examine nonlocal diffusion and dispersion. Phase transition were studied with MC and MD methods. New techniques were developed to compute the chemical potential of the vicinal phase. Interfacial tension was studied using GCEMC. Anomalous diffusion in monolayer films was analyzed via MD, scaling arguments and fractal Brown motion.			<b>94 2 08 140</b> 	
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**Toward a Molecular-Scale Understanding of Frost Heaving: Phase I**

**Final Report for Phase I**

by

**John H. Cushman**

**December 13, 1993**

**U.S. Army Research Office**

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## I. Statement of Problem

A fundamental understanding of the physical and chemical basis for frost heaving (Derjaguin and Churaev, 1978) is critically important to improving the design of structures for use in cold regions (Andersland and Anderson, 1978). The disruptive action of ice is one of the main causes of weathering in the cryosphere (Mazurov and Tikhonova, 1964). Thin, poorly understood, yet highly temperature-dependent, aqueous films adsorbed on micro fissures generate a two-dimensional disrupting pressure of tens to hundreds of kilograms/cm<sup>2</sup> and play a major role in rock weathering (Derjaguin, 1943). For over 200 years people have been studying the physical mechanisms of ice-lens formation, yet it is not well understood on the molecular level.

In many permafrost areas, especially along the coasts of the northern oceans and in continental regions of limited moisture, natural saline soils and artificially salinized soils are often used as the base for buildings or as materials for earthen structures. Recently many physico-chemical methods of controlling frost heaving have begun to be used (e.g. addition of sulfite alkalis). These methods are connected with the variation of the physico-chemical properties of the soil, its capacity for adsorption, its specific surface and surface structure, and the nature of its exchange cations. The ability to control heaving by physico-chemical methods has developed through trial and error; very little is known about the true molecular mechanisms governing the phenomenon (Voroshilov, 1978).

It has been postulated that the coexistence of solid and liquid phases of water in frozen fine-grained soils, and the phase transitions of water in them, arise from the fact that ice crystals are in equilibrium, not with ordinary water, but with water having a distorted structure, the molecules of which are so disoriented by surface forces that they are not capable of organizing into the ice structure (Ananyan, 1963a, b). A standard method of probing the structure of vicinal water is nuclear magnetic resonance. In particular the spin-spin relaxation time,  $T_2$ , gives information about the rate of orientational relaxation. At present, however, there is no theory permitting a precise correlation of experimentally observed  $T_2$ 's with the

molecular structure and motion in vicinal water; only qualitative correlations are possible. Thus, there is no concrete evidence to support the hypothesis that surface forces distort the structure of vicinal water. In fact, some researchers doubt its correctness (e.g. Chahal and Miller, 1965).

O'Neill and Miller (1985) have developed a model of frost heaving in coarse-grained materials based on irreversible thermodynamics and continuum mechanics. The model performs well qualitatively, reproducing many macroscopic features associated with the heaving problem. Their model assumes that "for whatever reasons, liquid water very close to a grain surface is attracted toward that surface and that the attractive force is greater for liquid than for air or ice...". It seems clear that an ice lens accretes liquid water that is transported from warmer to cooler regions through the liquid film surrounding the grain, but the molecular mechanism of this process has not been investigated. One of the points of our work was to examine at a microscopic (i.e. molecular) level the interactions between the surface of the grain, the film of fluid, and the surface of the (growing) lens. We wanted to study the molecular structure of the film, that is the distribution of water and solute molecules relative to the two surfaces, as well as the mechanism of transport within the film. Our preliminary findings will supplement the current (macroscopic) picture of frost heaving and help provide a fundamental basis for some of the assumptions upon which models such as that of O'Neill and Miller rest.

In an earlier work, Romkens and Miller (1973) postulate two possible osmotic transport mechanisms for thermally-induced regelation of ice. In these models an idealized soil grain (a spherical glass bead) migrates from a cooler to a warmer region. One model assumes water diffuses from the warmer to the cooler region because of a gradient in solute (salt) concentration. The rate of migration of the bead is proportional to the diffusion coefficient  $D$  and to the slope of the freezing-point depression curve, as well as to ratios of the thermal conductivities  $K$  of the bead, film, and ice. The other model posits an electrical double-layer which leads to a pressure (force) gradient and to an expression for the rate of migration that

depends on the viscosity  $\eta$ , among other quantities. On a macroscopic level, it is practically impossible to determine which model is correct. However, at a microscopic level it is a different story. By solving the classical equations (i.e. Newton's equations) we may follow the motion of individual water and solute molecules. Appropriate averages over these detailed motions yield the transport coefficients (e.g.  $D$ ,  $K$ , and  $\eta$ ) that are involved in the above-described macroscopic models. These transport coefficients depend, of course, on the microscopic properties of the materials making up the soil. Our studies yield information on some of this dependence, which in turn provides a fundamental basis for altering the properties in order to control the migration of particles and consequently the strength of frozen ground.

The advent of supercomputers has made it feasible to model frost heaving on a molecular scale. We have begun to delineate the true microscopic physical processes that take place when soils begin to heave upon freezing or shrink upon thawing, or when ice nucleates and ice lenses form. To do so requires a combination of expertise ranging from chemical physics to soil physics and from applied mathematics to vector programming.

## II. Summary of Important Results

### i. Thermomechanics

The thermomechanics of a multiphase multicomponent mixture are developed in the spirit of modern continuum physics. A new axiom of constitution, "equipresence of constituents", is stated and employed to obtain macroscale equations of constitution which are consistent with their microscale counterparts. Here we assume a scale separation wherein the classical microscale theory of mixtures applies within each phase and interface, and a hybrid theory of mixtures, which is a homogenization of the microscale mixture theory over phases and interfaces, applies at the macroscale. We thus postulate the existence of a two-scale hierarchy of overlaying continua. Such scale separation is common to many types of porous media.

Exploitation of the entropy inequality in the sense of Coleman and Noll and application of equilibrium constraints produces a complex list of functional relations forming a macroscale theory of constitution. In a three phase system linearization of several of these relations produces novel analogs of Fick's first law of diffusion and Darcy's law of fluid transport in deforming porous media. These analogs of Fick's and Darcy's laws are significantly different from their traditional forms in that they contain an "interaction potential". We feel that the contribution of the interaction potential to fluid flow dynamics could be of crucial importance in swelling and shrinking colloidal systems. Another especially important consequence of the theory of constitution is the development of the experimentally observed exponential relation between disjoining (swelling) pressure and the pore width in a smectitic clay-water system. This relation cannot be developed using classical Gibbsian thermostatics. Rational definitions of a nonequilibrium capillary pressure and a nonequilibrium swelling pressure are provided for the first item. The swelling pressure is found to be the pressure difference between the interfacial and bulk phase only at equilibrium. For the general nonequilibrium case, using a linear theory, an extra term in the material derivative of volume fraction is found in the swelling relationship. A similar relation is developed for nonequilibrium capillary pressure.

## ii. Nonlocal Dispersion

Molecular hydrodynamics and the associated theories of statistical mechanical equilibrium correlation functions are used to develop a spatially and temporally nonlocal convective-dispersive equation for transport in fractal porous media. A frequency and wave vector dependent dispersion tensor is developed from statistical mechanical principles. All results reduce to their classical Fickian counterparts under appropriate conditions. Expansion approximations of a spatially and temporally nonlocal convective-dispersive equation are introduced to derive linearized inverse solutions for transport coefficients.

A fully nonequilibrium statistical mechanical theory of transport which involves both diffusive and convective mixing (dispersion) at all scales was developed. The theory is based on a generalization of classical approaches used in molecular hydrodynamics and on time-correlation functions defined in terms a "nonequilibrium" expectations. The resulting constitutive laws are nonlocal and constitutive parameters are wavevector and frequency dependent. All results reduce to their convolution-Fickian, quasi-Fickian or Fickian counterparts in the appropriate limits.

## iii. Phase Transitions

Phase transitions in Lennard-Jones (LJ) and Stockmayer fluids confined between two parallel fcc (100) planes of rigidly fixed LJ atoms are studied by means of a mixed isostress-isostrain grand-canonical Monte Carlo methods, and a microcanonical ensemble molecular dynamics technique. A nonequilibrium continuum thermodynamic derivation of the constitutive laws for the basic slit-pore model is developed and an equilibrium statistical thermodynamics analog is reviewed. Independent constitutive parameters are chosen from the list  $T$ ,  $\mu$ ,  $\bar{E}_y$  or their thermodynamic duals  $\eta$ ,  $N$ ,  $\tau_y$  where  $T$  is absolute temperature,  $\mu$  is the chemical potential,  $\bar{E}_y$  is the infinitesimal strain tensor,  $N$  is the particle number,  $\eta$  is the entropy and  $\tau_y$  is the Piola stress tensor.



In all cases studied the pore fluid is in equilibrium with its bulk phase counterpart which is liquid. The local density and the cylindrical pair-correlation function in planes parallel to the walls, indicate that the structure of the pore fluid depends strongly on the distance  $h$  separating the walls (or the dual stress) and their lateral alignment (shear strain,  $\bar{E}_{31}$ ). The pore phase may be liquid, gaseous or solid depending on  $h$  (or  $\tau_{33}$ ), shear stress  $\tau_{31}$  (or  $\bar{E}_{31}$ ), and dipole moment, for fixed  $T$  and chemical potential. The additional degree of freedom provided by the dipole moment of the Stockmayer fluid strongly influences the structure of the pore fluid. As the moment increases, the degree of order of the pore fluid decreases.

Fluctuations of enthalpy and density in the isostress-isostrain ensemble are employed to accumulate evidence for shear strain induced melting (shear melting) to occur as a second order liquid-solid phase transition. Shear melting of a solid-like monolayer film in a model slit-pore is studied by means of an isostress-isostrain ensemble Monte Carlo (MC) method. Quantities of prime interest are isostress heat capacity  $c_3$ , isothermal compressibility  $\chi_3$  and isostress expansivity  $\gamma_3$ , where the subscript 3 references the component of stress normal to the pore walls. If studied as functions of lateral registry  $\alpha$  (as a measure of  $\bar{E}_{13}$ ), these quantities diverge at the shear melting point  $\alpha_c$  according to theoretical considerations. Theory also predicts a power law decay of  $c_3$ ,  $\chi_3$  and  $\gamma_3$  proportional to  $(\alpha - \alpha_c)^\nu$  for  $\alpha > \alpha_c$  where  $\nu$  is a critical exponent. Although fluctuations in enthalpy and density diverge at  $\alpha_c$ , enthalpy and density themselves remain continuous functions of applied strain everywhere. Thus, shear melting occurs without release of latent heat, which furnishes further evidence for a liquid-solid phase transition of second order.

#### iv. Chemical Potential

A new approach to the computation of chemical potential and free energy was developed. The basic idea is to correct the underestimate obtained by the particle-removal method. Application of the new technique to several different thermodynamic states of the

Lennard-Jones (12,6) fluid shows that it is capable of providing reliable estimates of the chemical potential, even at high density where standard methods encounter computational difficulties. This technique has been used extensively to obtain the chemical potential for a Stockmayer fluid. This is the first report of such data for this fluid.

#### v. Interfacial Tension

The grand canonical ensemble MC method has been used to study the interfacial tension in a rare-gas film confined to a slit-pore whose plane-parallel walls comprise rigidly fixed similar rare-gas atoms. In narrow pores, where both walls strongly influence the whole film, the interfacial tension is shown to be a highly complex function of pore width and transverse alignment of the walls. Oscillations in the tension are correlated with the addition of new fluid layers, the most highly structured layers corresponding to maxima in the tension. Separate interlayer and intralayer contributions to the tension are defined and shown to be useful in explaining the physics of the change in interfacial tension with the addition of new layers of the film.

#### vi. Anomalous Diffusion

A monolayer, solid, epitaxial film confined to a slit-pore and subjected to a shear strain begins to melt if a critical strain is exceeded. The resulting "molten" phase exhibits structural disorder characteristic of a liquid yet it supports a shear stress. MD and MC calculations were used to study self-diffusion in this molten phase as a function of excess shear strain above the critical value. Three distinct self-diffusion time scales are manifest through plots of the mean-square displacement (MSD). Over the shortest time scale the MSD can be represented by a power-law,  $\sim t^d$ , where  $t$  is time and  $d$  is a function of excess shear strain, varying from 0 for the solid just below the shear melting point to its Brownian-limit value of 1 for a completely liquified film, having the disorder of a bulk fluid and supporting no shear-stress. That  $d < 1$  indicates anomalous (i.e., non-Brownian) self-diffusion. The intermediate time scale is

characteristic of a strongly cooperative process that is spatially nonlocal and gives rise to anomalous diffusion. Both short and intermediate time scales exceed by several orders of magnitude typical times after which Brownian diffusion is observed in dense homogeneous bulk fluids. The persistence of anomalous diffusion is ascribed to severe spatial confinement of the film atoms. The longest time scale corresponds to asymptotic Brownian diffusion for which  $d = 1$ . All results are interpreted in terms of a model in which film atoms are diffusing in an effective molecular-scale porous medium generated by the potential field of the walls atoms.

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