

silicon concentration (unpublished work). A more likely explanation is that silicon, like indium, traps one or other point defect thereby enhancing the nucleation rate. We do not know at the moment why silicon promotes the nucleation of dislocation loops rather than voids.

The significance of these results is that it might be possible to control the nucleation of voids in reactor materials by suitable addition of a substitutional solute.

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Statistical Mechanics and the Anomalous Swelling of Aluminosilicate Clays

THE anomalous swelling of the vermiculite and montmorillonite clays is a long-standing problem in the field of colloid stability and is of great environmental importance. Suspensions of clay particles in aqueous electrolyte can be studied. These clay particles are made up of one dimensional stacks containing up to several hundred parallel sheets of diameter about 10^{-6} m and thickness 10^{-9} m. These stacks are observed to swell, that is, the average spacing between the plates increases when the concentration of electrolyte is decreased. It has been possible to measure both the average swelling of a stack of plates and the plate-plate distribution function $W(L)$ as functions of electrolyte concentration by scattering X-rays through low angles¹.

The DLVO theory of colloid stability may be used to calculate the equilibrium mean spacing in such an assembly as a function of electrolyte concentration, being the spacing at which the attractive van der Waals forces between the plates exactly balances the repulsive double layer forces. The double layer force between two plates is calculated from the measured zeta potential, interpreted as the potential at the outer Helmholtz plane (OHP). Friend and Hunter² have reported values of the zeta potential of vermiculite which inspire confidence because they are consistent with negative adsorption measurements. The recent application of the Lifshitz theory of van der Waals forces to multilayer systems³ has been extended to give a reliable estimate of the attractive forces in a vermiculite stack (J. W. Perram and B. W. Ninham, unpublished communication). The theory explains the experimental data adequately at high electrolyte concentration, but at low electrolyte concentration the calculated mean spacing is much greater than that measured. This deviation from experiment is known as "anomalous swelling".

This suggests either that the assumption that the zeta potential, measured for a single plate, is identical to the potential at the OHP of an interior plate in the stack is not correct, or that the view that the problem may be treated by a balance of forces between pairs of plates is too simple. We pursue the latter point of view and observe that the plate stack may be modelled by a one dimensional gas of hard rods under the influence of pairwise attractive (van der Waals) and repulsive (double layer) forces. This approach

will be meaningful, as the calculated potential curve has a minimum of depth of order kT .

The calculated energy curve has an attractive tail which behaves as $-L^{-2-\epsilon}$, where ϵ is small. This arises, rather than the retarded form $-L^{-3-\epsilon}$, because of the non-retarded nature of the contribution to the van der Waals forces due to microwave and infrared relaxation of the intervening water⁴. The repulsive component of the energy behaves as a hard core of the dimensions of a plate plus its attached Stern layer⁵, and a term proportional to $e^{-\kappa L}$, where κ is the Debye parameter for the electrolyte. At large separations, where the anomalies are most apparent, the energy curve is dominated by the attractive forces.

Statistical mechanical studies of the properties of one dimensional systems indicate that gross features, such as the presence or absence of ordering, are independent of whether one considers a lattice or hard rod system⁶. Recently, Dyson⁷ has studied the problem of whether a one dimensional Ising model with $-L^{-p}$ interactions has a phase transition to an ordered state. He showed that for $1 < p < 2$, such a phase transition occurs, but not if $p > 2$. This indicates that for $p = 2 + \epsilon$, where ϵ is small, the system will exhibit large order fluctuations. Interpreted for the case of vermiculite and montmorillonite, this means that there will be large numbers of clusters with long lifetimes. Because of the mass ($\approx 2.5 \times 10^{-18}$ kg) of the plates, this lifetime will be very large indeed.

In fact, such clustering is observed, as Barclay and Thompson have produced electron micrographs showing almost unexpanded clusters of about 3 plates⁸. This implies that neither of the above assumptions is justified. If the spacings between the plates are not uniform, which is also suggested by the diffuseness of $W(L)$ determined by X-ray scattering, then the potentials at the various OHPs will not be identical, nor equal to the measured zeta potential. Also, the van der Waals forces between the plates cannot be validly represented by a pairwise sum of interactions between plates³.

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Internal Friction Peaks due to Adsorbed and Capillary Water in Microporous Substances

DURING our continuing investigation of the dynamic mechanical response (DMR)—elasticity modulus E , and internal friction $\tan \delta$ —of microporous substances saturated with water, we have found two transitions in the temperature range from -140° to 25° C. The substances which we have examined are hardened cement