

INTERPARTICLE POTENTIAL ENERGIES IN Na-MONTMORILLONITE CLAY SUSPENSIONS*

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Abstract—The small angle X-ray scattering data obtained in an earlier investigation of a series of Na-montmorillonite clay samples containing varying concentrations of sodium metaphosphate have been used to calculate the potential energy $\phi(x)$ of the interaction between two isolated parallel clay platelets separated by a distance x . All $\phi(x)$ curves have the form expected for Na-montmorillonite. In each curve there is a potential well for a platelet separation approximately equal to the most probable separation distance determined in the earlier study. Because the depth of the potential well is of the order of 0.01 eV for all samples, the attractive forces are relatively weak. While the calculated $\phi(x)$ functions are not highly accurate, in future investigations precautions can be taken to increase the reliability of the computed potential energy functions. This preliminary study suggests that determination of $\phi(x)$ from small angle X-ray scattering data can be a useful method for quantitative study of interparticle forces in Na-montmorillonite clays.

INTRODUCTION

IN A RECENT investigation of interparticle interactions in Na-montmorillonite clay suspensions to which sodium metaphosphate had been added (Andrews, Schmidt and van Olphen, 1967), small angle X-ray scattering data were used to calculate the pair correlation function $g(x)$ which described the probability‡ that, in an aggregate of parallel platelets, the centers of two platelets would be separated by a distance x .

The information about interparticle forces, however, was obtained indirectly. These forces can often be studied more conveniently by considering the potential energy $\phi(x)$ of interaction of two isolated parallel clay platelets separated by a distance x .

The pair potential function $\phi(x)$ can be calculated from the experimental scattering data by use of the one-dimensional analogue of the three-dimensional theory employed in finding the pair potential from the small angle X-ray scattering data from southern bean mosaic virus suspensions (Schmidt and Taylor, 1967). We have recently used the scattering data of Andrews, Schmidt and van

Olphen to compute $\phi(x)$ for a series of Na-montmorillonite clay samples.

The pair correlation function $g(x)$ can be obtained from the scattering data by numerical evaluation of the equation (Andrews, Schmidt and van Olphen, 1967)

$$g(x) = 1 + (L/\pi) \int_0^\infty dh [i(h) - 1] \cos hx \quad (1)$$

where $h = 4\pi\lambda^{-1} \sin(\theta/2)$, λ is the X-ray wavelength, θ is the scattering angle,

$$i(h) = \frac{I(h)}{I_e N F^2(h)}$$

$I(h)$ is the scattered intensity, N is the number of scattering particles in the sample, $I_e F^2(h)$ is the scattered intensity that would be obtained from a single particle for the same experimental conditions that were used to measure $I(h)$, and L is a normalizing constant. This constant can be evaluated by noting that $g(0) = 0$ because of the finite thickness of the platelets. Then for $x = 0$, Eq. (1) gives§

$$L = -\pi \left\{ \int_0^\infty dh [i(h) - 1] \right\}^{-1} \quad (2)$$

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‡Our notation differs from the terminology of Andrews, Schmidt and van Olphen. The function which they called the probability density function $P(x)$ is identical to our pair correlation function $g(x)$.

§There is an error in Eq. (2) of Andrews, Schmidt and van Olphen. On the right side of the equation, the term containing the factor (L/π) should be positive, not negative. Also, the last two columns of Table 1 of their paper are incorrectly labeled. In the notation used in the rest of their paper, these values equal $L_1/2$, not L_1 .

To find $\phi(x)$, additional results from the theory of fluids are necessary. Some approximate theories express $\phi(x)$ in terms of $g(x)$ and a function $f(x)$, known as the direct correlation function. For a one-dimensional system like an aggregate of parallel clay platelets, $f(x)$ can be defined by the integral equation

$$g(x) - 1 = f(x) + (1/L) \int_{-\infty}^{\infty} dy f(x-y) [g(y) - 1]. \quad (3)$$

In (3), $g(x)$ and $f(x)$ are defined to be even functions of x .

Because the direct correlation function cannot be directly calculated from the properties of the system, Eq. (3) must be considered a definition of the direct correlation function $f(x)$ (Fisher, 1964). Nevertheless, a convenient interpretation of (3) can be obtained by noting that according to (3), the total interparticle correlation, which is described by $g(x)$, can be considered to be the direct correlation between two particles, given by $f(x)$, plus the superposition of the indirect correlations propagated from the first particle to the second through a third particle. With this interpretation, $f(x)$ can be expected to have a shorter range than $g(x)$ —that is, for large x , $f(x)$ decreases more rapidly than $g(x)$.

From (1) and the convolution theorem for Fourier transforms

$$f(x) = (L/\pi) \int_0^{\infty} dh \{1 - [i(h)]^{-1}\} \cos hx. \quad (4)$$

Thus, from (1) and (4), both $f(x)$ and $g(x)$ can be calculated from $i(h)$, which in turn is obtained from the experimental scattering data.

One of the most successful of the modern approximate theories of fluids is the Percus-Yevick theory. In the one-dimensional form of this theory (Wertheim, 1964).

$$\phi(x) = kT \ln [1 - f(x)/g(x)] \quad (5)$$

where k is Boltzmann's constant, and T is the absolute temperature.

After (1) and (4) have been used to compute $g(x)$ and $f(x)$ from the experimental data, the pair potential $\phi(x)$ can be found from (5).

Our calculations of the pair potential from the small angle X-ray scattering data for a one-dimensional system are analogous to the techniques used by Mikolaj and Pings (1965, 1967) to obtain the three-dimensional pair potential from large angle X-ray scattering curves for argon.

RESULTS AND DISCUSSION

The scattering data discussed by Andrews *et al.* (1967) were used to compute $g(x)$ and $f(x)$. These functions were substituted in (5) to give the pair potential $\phi(x)$. The clay and sodium metaphosphate concentrations are listed in Table 1. Figures 1, 2 and 3 show the $\phi(x)$ curves from Samples 1, 2 and 3. The curves for Samples 4 and 5 had essentially the same form as the curves in Figs. 1 and 3. For Sample 6 both the $I(h)$ and $\phi(x)$ curves were essentially identical to the corresponding curves for Sample 1. A sodium metaphosphate concentration of 0.005 N is evidently too low to have an appreciable effect on the interparticle interactions in these clays.

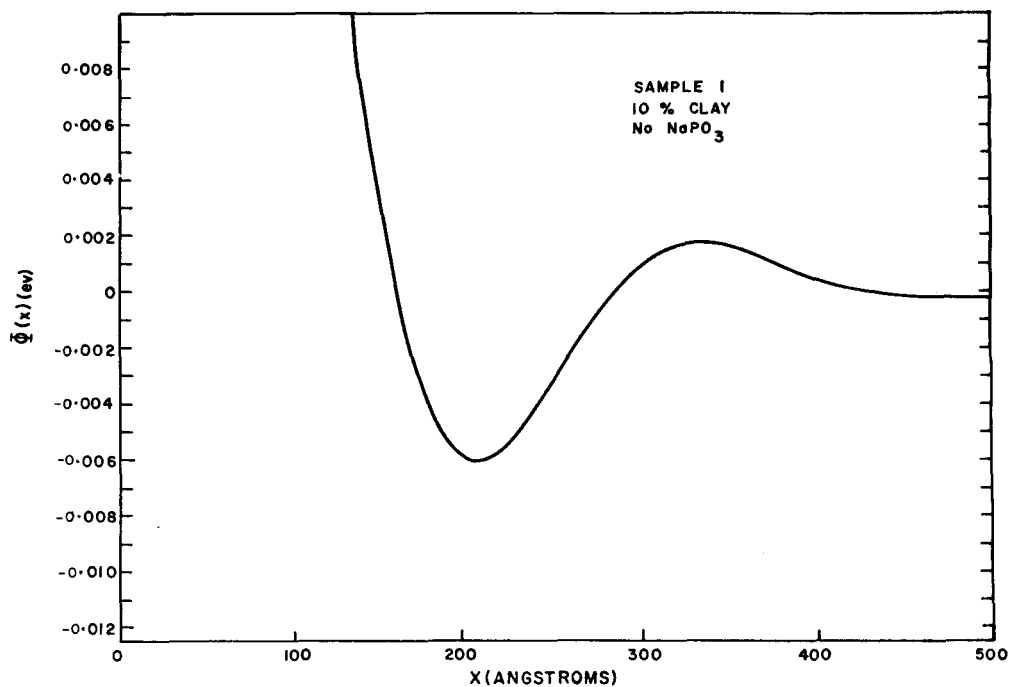
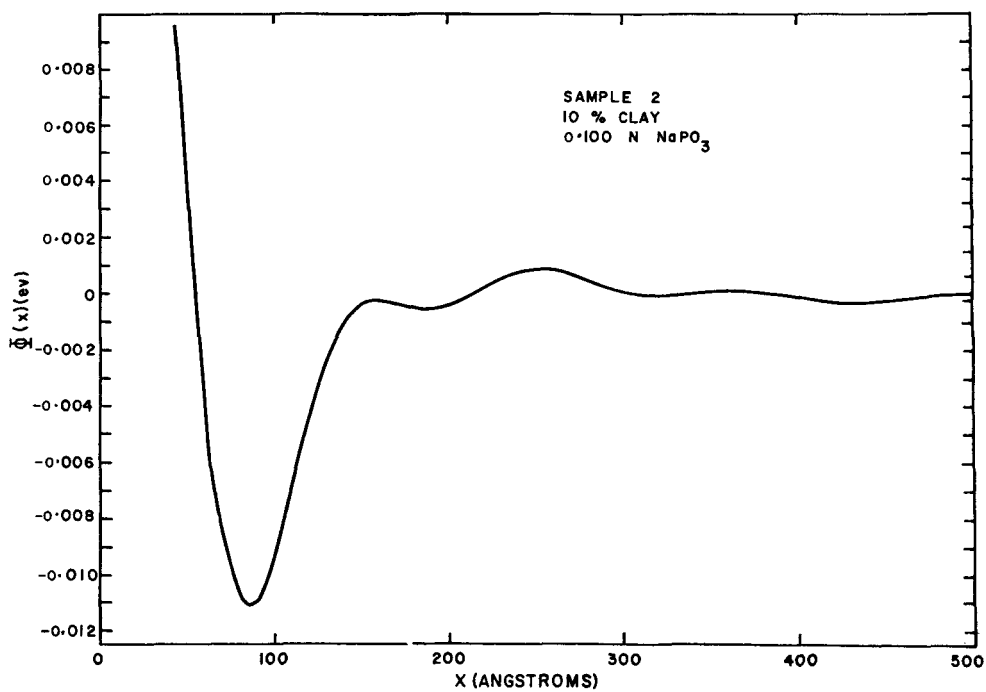
All pair potential curves have a similar form. For small x , $\phi(x)$ is large and positive and corresponds to a large repulsive force. As x increases, $\phi(x)$ becomes negative and has a minimum at a distance approximately equal to the equilibrium spacing between the platelets. For larger x , the pair potential becomes positive again and has a relatively low maximum. The function $f(x)$ then approaches zero as x becomes infinite. This behavior agrees qualitatively with the form of the pair potential generally considered to act between Na-montmorillonite particles.

Table 1 lists the positions d_* of the minima of $\phi(x)$ and gives the depths ϕ_* of the potential minima.† The values of d_* are very nearly equal to the equilibrium interplatelet distance d given by Andrews *et al.* (For comparison, these values

†The well depth ϕ_* is defined by the equation $\phi_* = \phi(d_*)$.

Table 1. Sample composition and values of d , d_* , and ϕ_*

Sample	Concentration (wt. %)	Concentration (eq/l)	d (Å)	d_* (Å)	ϕ_* (eV)
1	10	0	184	205	0.006
6	10	0.005	177	200	0.005
5	10	0.010	157	170	0.003
4	10	0.025	138	152	0.006
3	10	0.050	98	103	0.015
2	10	0.100	82	88	0.011

Fig. 1. The pair potential $\phi(x)$ for Sample 1.Fig. 2. The pair potential $\phi(x)$ for Sample 2.

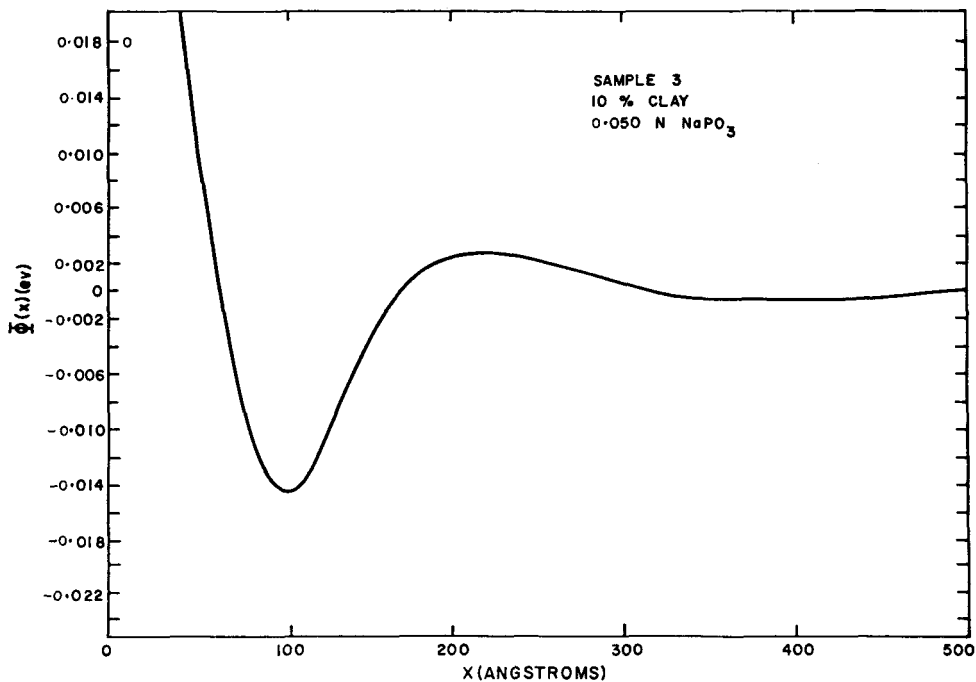


Fig. 3. The pair potential $\phi(x)$ for Sample 3.

are included in Table 1). Since the samples were studied at room temperature, $kT \sim 0.025$ eV. For all samples the well depths are of the order of 0.01 eV and thus are somewhat less than kT . The potential minimum therefore represents a relatively weak attractive force.

The positions d_* of the potential minima differ slightly from the equilibrium spacings d because the most probable distance between platelets in an assembly of parallel platelets is determined by other factors besides $\phi(x)$, which is the potential energy of interaction of a single pair of isolated platelets.

As the sodium metaphosphate concentration is raised, the position d_* of the potential minimum decreases, and there is a tendency for the well depth ϕ_* to increase. These changes would be expected from the compression of the diffuse double layers on the negatively charged faces of the particles which is caused by an increase of the sodium ion activity in the equilibrium solution.

The pair potential $\phi(x)$ can also be found from $g(x)$ and $f(x)$ by use of two other approximate theories, Taylor (1968). For the clay samples, all three theories were found to give essentially the same pair potential $\phi(x)$.

A definite limit cannot be set on the uncertainty in the values of $\phi(x)$. This function was calculated from integral transforms of functions obtained from

the experimental data. In this type of calculation, the relation between the final result and the initial data is so complicated that error bounds cannot be established. However, our experience indicates that the uncertainty in $\phi(x)$ is certainly greater than the uncertainty in the data points, which were accurate within at least a few per cent.

A number of tests were made to estimate the effect of uncertainties in the data, Taylor (1968). These tests showed that the overall shape of the $\phi(x)$ curves is almost certainly correct. This conclusion is supported by the qualitative similarity of the curves for the series of samples.

The absence of a single well-defined maximum in the $\phi(x)$ curve for Sample 2 is probably an artifact, and the weak maxima and minima in this curve for $x > 100$ Å are almost certainly artifacts.

The maximum of the $\phi(x)$ curve for Sample 5 was not as well-defined as in the curves for Samples 1, 3, 4 and 6. The lack of definition of this maximum probably is the result of an artifact.

The principal source of error in the $\phi(x)$ curves is the uncertainty in the form of $i(h)$ for small h , Taylor (1968). Evaluation of $g(x)$ and $f(x)$ required extrapolation of the $i(h)$ curves to $h = 0$. Equations (1) and (4) are Fourier cosine transforms, and the integrand is large in the neighborhood of $x = 0$. Since this part of the integrand makes a large contribution to the integral, the form of

$i(h)$ near $h=0$ has a relatively large influence on $g(x)$ and $f(x)$. To check the effects of extrapolation, several different extrapolations were used to compute $\phi(x)$ for the same sample. Large changes in $\phi(x)$ were found to be produced by unreasonably large variations of the extrapolation. The shape of the measured portion of the $i(h)$ curve, however, defined the extrapolation well enough to give meaningful $\phi(x)$ curves.

Although the position of the potential minimum was found to be affected only slightly by the extrapolation, the well depth was changed considerably. Since the well depth is so sensitive to the small- h extrapolation, the values of ϕ_* could be in error by 25% or more. Nevertheless, the trend of the ϕ_* values in Table I quite clearly suggests that the well depth increases with the concentration of sodium metaphosphate.

Because of the sensitivity of the $\phi(x)$ curve to the small- h extrapolation, in future measurements which are to be used for calculating the pair potential, the inner part of the scattering curve should be measured especially carefully, and attempts should be made to obtain data at h values as small as possible.

Just as in this calculation of the pair potential for a one-dimensional system, uncertainties in the scattered intensity can have relatively large effects on the three-dimensional pair potential obtained from the large angle X-ray scattering data from dense fluids. Verlet (1968, pp. 204–205) has considered some of the problems encountered in this type of calculation.

Our investigation indicates the feasibility of using small angle X-ray scattering to determine the form of the pair potential $\phi(x)$ for clays. This preliminary investigation has suggested procedures and techniques which can provide more reliable

values of the pair potential. These pair potential curves will be useful in providing an understanding of the nature of the forces acting in suspensions of clay particles.

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REFERENCES

- Andrews, D. E., Schmidt, P. W., and van Olphen, H. (1967) X-ray study of interactions between montmorillonite platelets: *Clays and Clay Minerals* **15**, 321–30.
- Fisher, M. E. (1964) Correlation functions and the critical region of simple fluids: *J. Math. Phys.* **5**, 952.
- Schmidt, P. W., and Taylor, T. R. (1967) Interparticle interactions in southern bean mosaic virus suspensions: *Physics of Fluids* **10**, 885–8.
- Taylor, T. R. (1968) Ph. D. Thesis, University of Missouri, Columbia, Missouri. Copies Available from University Microfilms, Ann Arbor, Mich, 48106, Order No. 69–3416. (Microfilm \$3.00, Xerox \$4.80.)
- Wertheim, M. S. (1964) Analytic solution of the Percus-Yevick equation: *J. Math. Phys.* **5**, 643.
- Mikolaj, P. G., and Pings, C. J. (1965) Direct experimental test of the Percus-Yevick and convoluted hypernetted chain integral equations: *Physical Rev. Letters* **15**, 849–52.
- Mikolaj, P. G., and Pings, C. J. (1967) Structure of liquids—IV. Direct correlation functions of liquid argon: *J. Chem. Phys.* **46**, 1401–12.
- Verlet, L. (1968) Computer “experiments” on classical fluids—II. Equilibrium correlation functions: *Phys. Rev.* **165**, 201–14.

Résumé—Les données de dispersion des rayons X à petit angle obtenues dans une étude précédente d'une série d'échantillons d'argile Na-montmorillonite contenant des concentrations variables de métaphosphate de sodium ont été utilisées en vue de calculer l'énergie en puissance $\phi(x)$ de l'interaction entre deux platelets isolés et parallèles d'argile, séparés par la distance x . Toutes les courbes $\phi(x)$ ont la forme que l'on attend du Na-montmorillonite. Dans chaque courbe il existe un puits potentiel pour la séparation de platelets à peu près égal à la distance de séparation la plus probable déterminée selon l'étude précédente. Etant donné que la profondeur du puits potentiel est de l'ordre de 0,01 eV pour tous les échantillons, les forces d'attraction sont relativement faibles. Tandis que les fonctions calculées de $\phi(x)$ ne sont pas hautement précises, on pourra—dans le cas d'études ultérieures—prendre des précautions en vue d'augmenter la précision des fonctions d'énergie potentielle calculées. Cette étude préliminaire suggère que la détermination de $\phi(x)$ à partir des données de dispersion des rayons X à petit angle peut présenter une méthode utile pour une étude quantitative des forces inter-particule dans les argiles Na-montmorillonite.

Kurzreferat—Die bei einer früheren Untersuchung einer Reihe von Na-Montmorillonitproben mit verschiedenen Konzentrationen an Natriummetaphosphat mit kleinwinkliger Röntgenstrahlung erhaltenen Streuungsdaten wurden verwendet um die Potentialenergie $\phi(x)$ der Wechselwirkung zwischen zwei, durch eine Distanz x von einander getrennten, parallelen, Tonplättchen zu berechnen. Alle die $\phi(x)$ Kurven haben die für Na-Montmorillonit erwartete Form. In jeder Kurve besteht eine

Potentialvertiefung entsprechend einer Plättchendistanz, die ungefähr der in der früheren Untersuchung bestimmten Trennungsdistanz gleich ist. Da die Tiefe der Potentialvertiefung bei allen Proben in der Grössenordnung von 0,01 eV liegt, sind die Anziehungskräfte verhältnismässig schwach. Die errechneten $\phi(x)$ Funktionen sind zwar nicht sehr genau, doch sollte es in zukünftigen Untersuchungen möglich sein Massnahmen zu treffen um die Zuverlässigkeit der errechneten Potentialenergiefunktionen zu erhöhen. Diese vorläufige Untersuchung zeigt, dass die Bestimmung von $\phi(x)$ aus kleinwinkligen Röntgenstreuungsdaten eine brauchbare Methode für eine quantitative Untersuchung der Zwischenteilchenkräfte in Na-Montmorillonittonen darstellen kann.

Резюме—Данные о распространении рентгеновских лучей под малым углом, полученные в ходе проведенного в прошлом исследования образцов Na-монтмориллонитовых глин, содержащих различные концентрации метафосфата натрия, применялись, чтобы высчитать потенциальную энергию $\phi(x)$ взаимоотношения между двумя выделенными параллельными глинистыми пластинками, отделенными расстоянием x . Все кривые $\phi(x)$ имеют форму, которая предвидится для Na-монтмориллонита. В каждой кривой имеется потенциальная яма для отделения пластинок, которая пригл. равна наиболее правдоподобию расстоянию разделения, определенному в более предыдущем исследовании. Силы притяжения сравнительно слабы из-за того, что глубина потенциальной ямы порядка 0,01 эв для всех образцов. В то время как вычисленные функции $\phi(x)$ не есть очень точными, в будущих исследованиях можно будет принять меры предосторожности для повышения надежности вычисленных функций потенциальной энергии. Настоящее предварительное исследование наводит на мысль, что определение $\phi(x)$ на основании данных распространения рентгеновских лучей под малым углом, может быть полезным методом для количественного исследования межчастичных сил в Na-монтмориллонитовых глинах.