JOURNAL OF MATERIALS SCIENCE 23 (1988) 3958–3962

Formation of solid–liquid interface in ferroelectric particle dispersion and its effect on the dispersion stability

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A model has been proposed for the formation of the ferroelectric solid–liquid interface in the non-electrolyte dispersion system. Bulk properties as well as the surface properties of the dispersing solid could be a factor which was associated with various characters of the dispersion state. A qualitative investigation was carried out to see whether the continuum polarization process in solid–liquid interface due to the inhomogeneous field from the polar solid might affect the powder dispersion. The development of the polarized solid–liquid interface might depend on the polarity of solid particle and of liquid medium, shapes, mobility, and solubility of the molecules in the liquid phase, and temperature. Two possible effects of polarized solid–liquid interface on the dispersion stability have been discussed. Lastly, this model was applied to interpreting some experimental results of adhesion.

1. Introduction

The various characters of suspension in ceramic processing directly affect the final properties of many products because the degree of dispersion, stability, and rheological properties critically control the microstructures and dimensions of the sintered body. Therefore, a fundamental understanding of the properties of the colloidal state is a prerequisite.

Recently, considerable progress has been made on the dispersion of inorganic oxide systems. Parfitt [1] considered the dispersion process as a wetting powder, breaking up the clusters, and stability. Some properties of a capacitor oxide powder dispersion in several classes of pure organic liquids were reported by Parish *et al.* [2]. They found that the hydrogen bonding capabilities of dispersion medium were an important factor in determining the degree of dispersion; good hydrogen bonding liquids dispersed the oxide powders much better than the poor or non-hydrogen bonding liquids.

The mechanism responsible for the high value of the dielectric constant of ferroelectric materials is the orientation polarization of permanent dipoles, which possess a dipole moment in the absence of an external field [3, 4]. It is natural to expect that the presence of groups of some large permanent dipole moment in a particle of the disperse system will affect the colloidal system. The existence of a permanent dipole moment associated with suspension particles was noted by some investigators [5–7], but in the majority of cases its nature is unclear.

Parsegian and Ninham [8] introduced a model for the van der Waals interaction in a lipid–water system from the dielectric permeabilities of the materials, where the relationship between the formation of interlayer and free energy was expressed and a dielectric continuum model in the interface was proposed. Parsegian and Weiss [9] reported that the dielectric susceptibility at the lipid–water interface could be a continuously varying function of position. The electric potentials of the ferroelectric particles from the enormous oriented permanent dipoles, which lie in the direction as the molecules consisting of dispersing medium are physically interacting, have a position function from the solid surface. Thus, it is possible to make a qualitative model for the formation of a polarized continuum interface of the ferroelectric solid–liquid interface in the non-electrolyte dispersion system. Our model is used to explain some experimental results of adhesion.

2. Polarization of liquid solution surrounding a ferroelectric solid particle

Non-electrolyte solutions consisting of polar molecules in colloidal systems are quite common in our experience, but there is no generally acceptable explanation. A thermodynamic model which treated dipole–dipole and dipole–induced dipole interactions, based on Onsager's model for the static dielectric constant, was developed by Haskell [10]. However, this model did not include the effects of dispersion forces and association, thus practical comparison was not possible. Madden and Klvelson [11] developed a molecular theory for the dipolar torque on a rotating molecule in a polar medium and showed how the molecular expression might be reduced to the continuum results. Two effects resulting from dipolar interaction are the enhanced two-particle equilibrium orientational correlations and the dipolar torques

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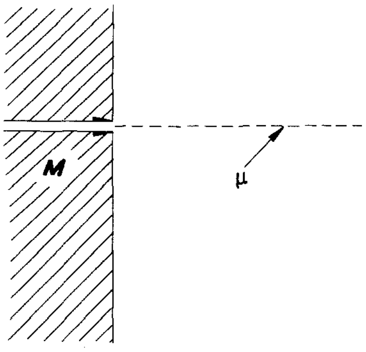

Figure 1 The polarization of the liquid environment of the polar solid.

which arise from the slow relaxation of the reaction field or of the dipolar torques on a given molecule.

When a ferroelectric crystalline solid is immersed in a liquid medium, an electric field due to the spontaneous polarization of the solid is exerted on the molecules of liquid medium as the inhomogeneous field in the same range. From potential theory, we know that if div $\boldsymbol{E} = \varrho$, and if curl $\boldsymbol{E} = 0$, then $\boldsymbol{E} = -\nabla\varrho$, where $\varphi(r)$ is the potential due to a localized charge distribution $\varrho(\boldsymbol{r}')$

$$\varphi(\boldsymbol{r}) = \int_{\tau'} \frac{\varrho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{d}\tau' \tag{1}$$

The charge of density $\varrho(\boldsymbol{r}')$ is localized in a volume τ'. To calculate the field at position $\boldsymbol{r}$, remote from the source for $|\boldsymbol{r}| > |\boldsymbol{r}'|$, we expand R^{-1} ($\equiv|\boldsymbol{r} - \boldsymbol{r}|^{-1}$) in powers of r'/r. The resulting equation is

$$\frac{1}{R} \equiv \frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|} = \frac{1}{r}\sum\left(\frac{r'}{r}\right)^n P_n(\cos\theta) \tag{2}$$

where $P_n(\cos\theta)$ are the Legendre polynomials,

$$\begin{aligned} P_0(\cos\theta) &= 1, \\ P_1(\cos\theta) &= \cos\theta, \\ P_2(\cos\theta) &= \tfrac{1}{2}(3\cos^2\theta - 1), \text{ etc.} \end{aligned} \tag{3}$$

If we substitute the expansion of $\boldsymbol{R}^{-1}$ into the expression for $\varphi(r)$, we have

$$\begin{aligned} \varphi(r) = {} & \frac{1}{r}\int_{\tau'} \varrho(\boldsymbol{r}')\,\mathrm{d}\tau' + \frac{\boldsymbol{r}}{r^3}\cdot\int_{\tau'} \boldsymbol{r}'\varrho(\boldsymbol{r}')\,\mathrm{d}\tau' \\ & + \frac{1}{2}\frac{x_i x_j}{r}\int_{\tau'} (3x'_j x'_j - \delta_{ij}\boldsymbol{r}'^2)\,\varrho(\boldsymbol{r}')\,\mathrm{d}\tau' + \cdots \end{aligned} \tag{4}$$

where the second term is the potential due to the dipoles distribution in volume. Here, as the component, r_x, perpendicular to the surface is of importance, we consider the electric field intensity at a position along the r_x direction (Fig. 1).

Thus

$$\boldsymbol{E}_\mathrm{s} = -\nabla\varphi = -\frac{-2M}{r_x^3} \tag{5}$$

where M is $\int_{\tau'} \boldsymbol{r}'\varrho(\boldsymbol{r}')\,\mathrm{d}\tau'$ and $\boldsymbol{E}_\mathrm{s}$ the electric field from solid.

The field of Equation 5 due to the enormous aligned dipoles in the same direction in ferroelectric solid affects behaviour of the molecules of liquid phase surrounding the solid surface.

It is useful to have an expression for the change in the free energy of the dielectric upon application of the field. Following Frohlich the energy of a particle in an external field will be given by equation 6

$$\Delta W = -\tfrac{1}{2}\alpha\boldsymbol{E}_\mathrm{s}^2 \tag{6}$$

When a molecule is brought into an electric field, the dipole moment will change. If the dipole moment of the particle in the absence of an electric field is denoted by $\boldsymbol{\mu}$ and the total moment when the field has been applied by $\boldsymbol{m}$, we may write the induced dipole moment $\boldsymbol{p}$ as

$$\boldsymbol{p} = \boldsymbol{m} - \boldsymbol{\mu} \tag{7}$$

The induced dipole moment $\boldsymbol{p}$ will be a function of the applied field strength $\boldsymbol{E}_\mathrm{s}$. For isotropic particles the induced moment will have the same direction as the applied field, so that we may write

$$\boldsymbol{p} = \alpha\boldsymbol{E}_\mathrm{s} \tag{8}$$

where α is the polarizability.

When a molecule with zero net charge and permanent dipole moment $\boldsymbol{\mu}$ is placed in an external field $\boldsymbol{E}_\mathrm{s}$, the amount of work necessary to accomplish this will not be given solely by the potential energy V_m of the total moment in the external field. The work of polarization W_pol has to be expended to form the induced dipole against the internal force of molecule. Thus we may write

$$W = V_\mathrm{m} + W_\mathrm{pol} \tag{9}$$

where $V_\mathrm{m} = \boldsymbol{m}\cdot\nabla\phi(\boldsymbol{r}) = -\boldsymbol{m}\cdot\boldsymbol{E}(\boldsymbol{r})$.

When there is equilibrium between the external and internal forces working on the microscopic charges, the energy of the molecule will be

$$\mathrm{d}W = 0 \quad \forall\,\mathrm{d}\boldsymbol{p} \tag{10}$$

Hence,

$$\mathrm{d}W_\mathrm{pol} = -\mathrm{d}V_\mathrm{m} = \boldsymbol{E}_\mathrm{s}\cdot\mathrm{d}\boldsymbol{p} \tag{11}$$

From the proportionality relation ($\boldsymbol{p} = \alpha\boldsymbol{E}_\mathrm{s}$),

$$\mathrm{d}W_\mathrm{pol} = \frac{1}{\alpha}\boldsymbol{p}\cdot\mathrm{d}\boldsymbol{p} = \frac{1}{2\alpha}\mathrm{d}(\boldsymbol{p}^2) \tag{12}$$

Equation 12 leads to

$$W_\mathrm{pol} = \int \mathrm{d}W_\mathrm{pol} = \frac{1}{2\alpha}\int_0^p \mathrm{d}(\boldsymbol{p}^2) \tag{13}$$

and several equivalent forms

$$W_\mathrm{pol} = \frac{1}{2\alpha}\boldsymbol{p}\cdot\boldsymbol{p} = \tfrac{1}{2}\boldsymbol{p}\cdot\boldsymbol{E}_\mathrm{s} = \tfrac{1}{2}\alpha\boldsymbol{E}_\mathrm{s}\cdot\boldsymbol{E}_\mathrm{s} \tag{14}$$

Therefore, for the amount of work necessary to bring the molecule into an external field

$$\begin{aligned} W &= -(\boldsymbol{\mu} + \boldsymbol{p})\cdot\boldsymbol{E}_\mathrm{s} + \tfrac{1}{2}\boldsymbol{p}\cdot\boldsymbol{E}_\mathrm{s} \\ &= -\boldsymbol{\mu}\cdot\boldsymbol{E}_\mathrm{s} - \tfrac{1}{2}\alpha\boldsymbol{E}_\mathrm{s}^2 \end{aligned} \tag{15}$$

Equation 15 for the energy of a polarizable particle with a permanent dipole moment shows that the energy is a function of the position and the orientation of the particle with respect to the field. Thus the force exerted by an external field $\boldsymbol{E}_\mathrm{s}$ on a particle with permanent dipole moment $\boldsymbol{\mu}$ and polarizability α can be obtained

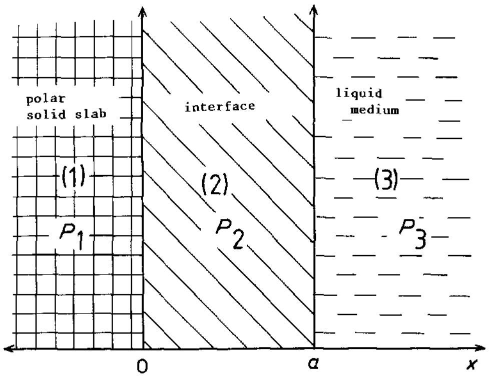

Figure 2 Semi-infinite model of the polarized solid–liquid interface "2" between polar solid slab "1" and liquid medium "3".

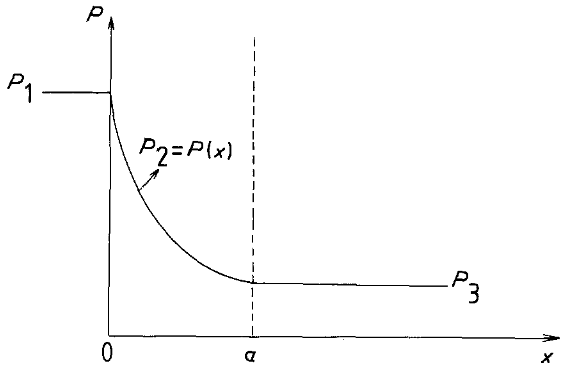

Figure 3 The intensity relation of polarization across solid–liquid interface for $P_1 \gg P_3$.

by taking the derivative of Equation 15

$$F = -\nabla W = \mu \cdot \Delta E_s + \alpha E_s \cdot \nabla E_s \quad (16)$$

This indicates that the translational force is proportional to the gradient of the external field and in an inhomogeneous field the particle will move in the direction given by Equation 16.

3. Model of ferroelectric solid–liquid interface

It has been mentioned that the electric field due to the permanent dipole is inhomogeneous and that in an inhomogeneous field the degree of polarization of environment can be dependent on the position from field source. This relationship leads to a model of polarization at the polar solid–liquid interface. Here we define the formation of the polarization viewpoint. When solid phase (1) with polarity, P_1, contacts with liquid phase (3) with polarity, P_3, then we assume that the interface, phase (2) with polarity $P_2(x)$, is formed between phase (1) and phase (3), where $P_2(x)$ is a function of position. The degree of polarization across the interface region will decrease since the external field, E_s, from the polar solid is inversely proportional to the position, so that at some distance, a, the effect of field, E_s, on environmental polarization is negligible. Therefore we may put the thickness of the polarized interface "a". Then we can set the boundary condition in Fig. 2

$$\frac{\partial P_1}{\partial x} = 0, \quad \frac{\partial P_3}{\partial x} = 0 \quad \text{when } x < 0, x > a$$

and (17)

$$\frac{\partial P_2}{\partial x} = P_2(x) \qquad \text{when } 0 < x < a$$

Assuming $P_1 \gg P_3$, we make a schematic curve of the polarization degree across the interface as a function of position (Fig. 3). Equations 5 and 16 show that the field from the solid is inversely proportional to x^3 and that the translational force is proportional to the gradient of the external field, but these relationships are limited to dipole–dipole and dipole–induced dipole interactions. However, in actuality, the formation processes of the polarized interface are more complex, that is, behaviour of the molecules of liquid media do not depend on only electrical forces. Various factors, for example, the shapes and mobilities of particles in liquid media, temperature, and so on, will directly effect on interfacial polarization process. So we simply postulate Equation 18 which describes the degree of polarization, $P_2(x)$, as inhomogeneous external field, E_s, exerts in liquid media in the x direction

$$\frac{\mathrm{d}P}{\mathrm{d}x} = -\gamma P \quad (18)$$

where γ is the attenuation constant of polarization.

γ is dependent on not only field intensity but also the shapes and mobilities of molecules in liquid media and temperature. Integration of Equation 18 gives

$$P(x) = P_0 \exp(-\gamma x) \quad \text{when } 0 < x < a \quad (19)$$

If the boundary condition of Equation 17 is applied to Equation 19

$$\text{(i) } x = 0, \quad P(0) = P_0 = P_1$$

$$\text{(ii) } x = a, \quad P(a) = P_1 \exp(-\gamma a) = P_3 \quad (20)$$

Then, an equation for the thickness of polarized interface can be derived

$$a = \frac{1}{\gamma} \ln \frac{P_1}{P_3} \quad (21)$$

Equation 21 indicates that the thickness of the polarized interface depends on the ratio of the polarities of the solid slab and of the liquid medium. In the fixed liquid medium system, the variation of inhomogeneously polarized interface length with changes of the polarity of solid slab can be shown (Fig. 4). Here it should be mentioned that even the postulate of Equation 18 does not have a quantitative foundation, Equation 21 might be physically convincible.

4. Effect of polarized interface on the stability of colloidal dispersion

The balance of interaction forces between colloidal particles determines whether a colloidal dispersion remains stable or undergoes flocculation. Van der Waals attraction is always present and the repulsion arise from electrostatic and/or absorbed large molecules the so-called steric effect [13, 14]. The total potential energy, V_T, of the interaction can be written as

$$V_T = V_A + V_R + V_S \quad (22)$$

where V_A is the van der Waals interaction energy,

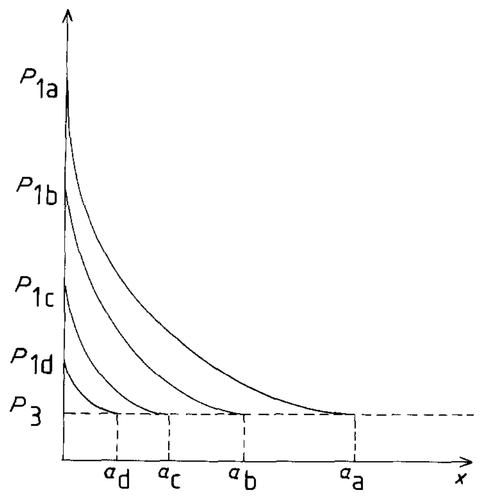

Figure 4 Change of the polarized solid–liquid interface thickness with variation of the polarities (P_1) of solid slabs in the fixed liquid medium (polarity P_3). $a = (1/\gamma)\ln(P_1/P_3)$.

V_R the electrostatic repulsion and V_S the interaction energy between particles due to the steric effect.

Under the condition of absence of free charges, the stability of colloidal dispersions will mainly depend on van der Waals forces and steric interactions. Here we investigate how our polarized model can contribute to the colloidal stability.

Fig. 5 shows the geometrical interaction between two particles with a polarized interface. As the gradient polarized interfaces are built up by the environment polarization process due to the inhomogeneous field from polar solid particle, some changes of intermolecular forces in the polarized interface region take place. According to London or dispersion, Debye or induction, Keesom or dipole [15], and hydrogen bond theories [16, 17], the free energy of adhesion, ξ_{SL}, is

$$\xi = -r^{-6}\left(\frac{3}{4}\alpha_1\alpha_2\frac{2I_1I_2}{I_1+I_2} + \frac{(\alpha_1\mu_1^2+\alpha_2\mu_2^2)}{2} + \frac{\mu_1^2\mu_2^2}{3kT}\right) \tag{23}$$

where α is mean electric polarizability, μ the permanent electric dipole moment, I the ionization energy, k the Boltzmann constant and T the absolute temperature.

Therefore, the attractive forces between molecules of the liquid belonging to the polarized interface are increased greatly. During interfacial polarization macromolecules may move in the interfacial region due to electrostatic attraction by the gradient field, Equations 5 and 16 and become more strongly bonded and concentrated near the solid particle. This may result in a loss of entropy, an increase of the free energy, and, thus, in a repulsion. In this way, the polarized interface will contribute to the stabilization of the colloidal particles with an increasing steric barrier.

Conversely, however, interfacial polarization can lead to inducing instability in disperse system. If the polarized interfaces (Fig. 5), in which polymeric molecules are concentrated overlap, molecules in the overlapped region are under the influence of the field from neighbouring particles. This can promote the formation of electrostatic bridging the molecules to cause the flocculation of dispersing particles.

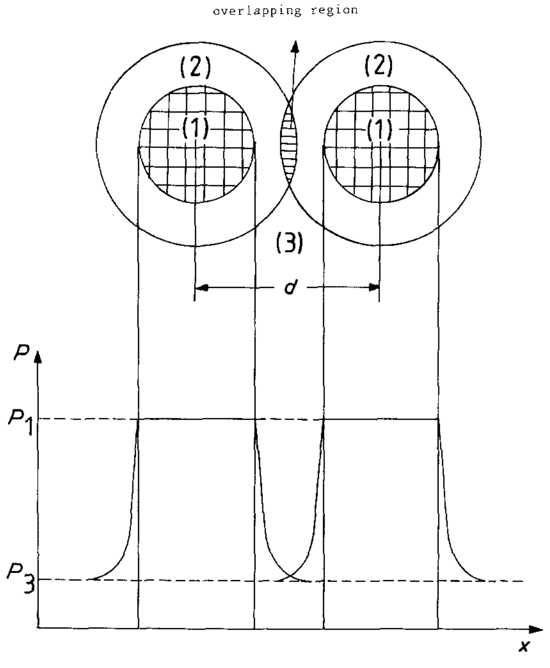

Figure 5 (a) Pair interaction between solid particles covered with polarized interface. (b) Overlapping scheme of inhomogeneously polarized interfaces. (1) polar solid particle, (2) polarized interface, (3) liquid medium, d distance between solids.

5. Experimental

Three types of oxide powders having different dielectric properties were dispersed in 5% polyvinyl butyral (PVB) solution containing mixed solvent (toluene(80)+ethanol(20)) with the same solid–liquid volume ratio. Each dispersion was then applied onto the high density polyethylene film(HDPE) and onto the polyethyene telephthalate film(PET) with uniform thickness, about 100 μm, using tape caster and then dried passing through the IR heating chamber. The resulting adhesion relation between the dried oxide film (thickness 50 μm) and carrier film (HDPE, PET) is shown in Table I.

TABLE I

Film	Powder		
	Type I ε_r = 6000	Type II ε_r = 2500	Type III ε_r = 100
HDPE (ε_r = 2.3)	Separated	Weak	Moderate
PET (ε_r = 3.1)	Weak	Moderate	Strong

ε_r is the relative dielectric constant.
Type I and type II powders have ferroelectric properties and their main constituent is BaTiO.

From Table I, it was shown that as the dielectric constant of dispersing powder increases, the resulting adhesion strength decreases. Here PVB molecules dissolved in dispersion play a key role in the adhesion results, that is, it depends on how many PVB molecules form linkages between the oxide film and HDPE or PET film.

In the following way, the above adhesion results might be related to our interfacial polarization model.

From Equation 21 and Fig. 4, in the fixed liquid media as the polarity of solid particle increases, the polarized interfaces are more extensively developed. Then PVB molecules participating in the polarized interface become less mobile as the molecules are restricted around the solid particle due to the dipole–dipole interaction. As a result, it is expected that dissolved PVB molecules are less likely to make an adsorption on the HDPE film. In this case, after the dispersion dried, the adhesion strength of the upper layer on HDPE film is too weak to endure the stress caused by drying shrinkage – type I. On the contrary, for the dispersion powder with low polarity (type III), dipole–dipole interaction forces between PVB molecules and solid particles are much lower. This may allow a high mobility of PVB molecules in the dispersion, compared with type I. Therefore, the adsorption density of the PVB molecules on the HDPE film is high enough to give strong adhesion.

6. Summary

In the manner of the continuum approach, a model is made for the development of the inhomogeneously polarized solid–liquid interface. The bulk properties of the dispersing solid particle might affect the environment of the solid. As some materials like ferroelectrics possess a dipole moment in the absence of an external field, their bulk properties, polarity, are probably associated with the dispersion states by dipole–dipole interactions. An attempt is made to estimate the possible effect of the formation of the polarized solid–liquid interface on a solid particle dispersion. Polymeric molecules may move to the interfacial region due to electrostatic attraction to be more strongly bonded and to be concentrated near the solid particles. As a result, the polarized interface can contribute to the stabilization of colloidal particles with an increasing steric barrier. On the other hand, under the influence of the field from neighbouring particles, bridging of macromolecules may be more actively formed to cause the fluctuation of the dispersing particles.

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Received 30 April 1987
and accepted 23 February 1988