

On the Equilibrium Thickness of Intergranular Glass Phases in Ceramic Materials

DAVID R. CLARKE*

Thomas J. Watson Research Center, IBM, Yorktown Heights, New York 10598

The fundamental question as to whether thin intergranular films can adopt an equilibrium thickness in polycrystalline ceramics is addressed. Two continuum approaches are presented, one based on interfacial energies and the other on the force balance normal to the boundary. These indicate that there will exist a stable thickness for the intergranular film and that it will be of the order of 1 nm. The origin of an equilibrium thickness is shown to be the result of two competing interactions, an attractive van der Waals-dispersion interaction between the grains on either side of the boundary acting to thin the film and a repulsive term, due to the structure of the intergranular liquid, opposing this attraction. As both of these interactions are of short range (<10 nm), it is a natural consequence that the equilibrium thickness is of the order of 1 nm, a value commensurate with that observed experimentally in a wide range of ceramics. Two further consequences of importance are indicated. The first is that thin intergranular liquid phases can support a normal stress. The second is that the dielectric constants of the adjacent grains play an important role in determining the thicknesses of the intergranular phase. This leads to the conclusion, consistent with observations, that the thickness of the intergranular phase in polyphase ceramics is expected to be different at boundaries between dissimilar phases than that between like phases.

I. Introduction

ONE of the most revealing findings produced during the examination of ceramic microstructures using the techniques of high-resolution transmission electron microscopy has been the fact that many of these materials contain a thin intergranular (generally siliceous) glass phase.¹⁻⁶ The thickness of the intergranular glass phase can be quite small, being ≈ 0.5 to ≈ 2 nm in some silicon nitride and zirconia ceramics and upward of ≈ 5 nm in some alumina-based materials. In the majority of materials the intergranular phase is both continuous throughout the microstructure and, significantly, located at the two-grain junctions.

As presently understood, the presence of a remnant intergranular glass phase can be produced by a number of different processes. In many ceramics, the phase results from the liquid-phase sintering process used to densify them. Examples of these include the silicon nitride alloys, the zinc oxide varistor materials, and alumina substrate materials. In others, such intergranular films are present because the materials are prepared by the controlled but incomplete crystallization of a glass (glass-ceramics). A third, but practically important, category is that in which the phase forms from the impurities present in the starting materials. For instance, a number of the ceramics developed for nuclear waste encapsulation⁴ and certain of the polycrystalline, tetragonal zirconia ceramics⁵ contain such intergranular films.

The purpose of the present paper is to address the question as to why the thickness of thin intergranular phases observed in many polyphase ceramic materials appears to be of a relatively constant value and why that value is of the order of 1 nm. A succeeding contribution will be devoted to the question of the stability of such thin intergranular phases and the mechanisms by which they may retract from grain boundaries. The work described in this contribution assumes that the intergranular phase wets the boundaries, meaning that it is energetically favorable for the phase to exist at the grain boundaries.

Following a brief review of the principal observational findings (Section II), an interfacial energy treatment is presented that provides a general conclusion as to the stable thickness of an intergranular phase. The presentation is based on well-established findings of the classical, van der Waals theory of liquids as presented by Widom^{7,8} and de Gennes.⁹ In Section IV, the individual forces acting normal to a thin intergranular fluid film between two grains are considered. It is shown that for a stable film thickness to exist the attractive force* due to the long-range van der Waals-dispersion interactions between the grains must be balanced by a net repulsive force, which is attributed here to a structural or steric interaction. Then a specific structural model is presented that provides for a physical origin of the structural force. In Section V an estimate of the thickness of a silica intergranular phase in alumina is presented. Finally, in Section VI the conclusions of the work and its implications for future observational tests are discussed.

Throughout this paper it is assumed that the intergranular phase acts as a liquid phase and adopts an equilibrium thickness at high temperatures. It is envisaged that, as in the majority of liquid-phase sintered ceramics where solution-precipitation phenomena occur, the thickness of the intergranular phase decreases as the grains grow toward one another until an equilibrium value is attained. Further, it is assumed that the pertinent microstructural features of the phase are frozen in when the materials are cooled for subsequent examination at room temperature by, for instance, transmission electron microscopy.

II. Observations

It has long been argued, on the basis of observations, using optical and scanning electron microscopy, of apparent zero contact angles measured in polished sections, that second phases can exist as thin intergranular films at grain boundaries. However, it was not until the advent of high-resolution electron microscopy techniques that it was unequivocally demonstrated that they existed along grain boundaries or their thicknesses were measured directly.¹⁻³ Observations reveal that the major fraction of intergranular phase is located at the intersections of three grains (triple junctions) and at four-grain junctions. Higher-resolution techniques further indicate that the majority of grain boundaries (two-grain junctions) contain a thin film of intergranular material. As the boundaries in more and more ceramics are scrutinized by transmission electron microscopy techniques, a greater number of materials are found to contain an intergranular phase. Such thin intergranular phases have been reported not only in the silicon nitride alloys in which their presence was first confirmed but also in a number of zinc oxide varistor ceramics, certain silicon carbides, capacitor dielectrics, (single-phase tetragonal and partially stabilized) zirconia ceramics, glass-ceramics, nuclear waste ceramics and aluminas, including many substrate-grade aluminas. Intergranular films have also been

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*Member, the American Ceramic Society.

*In the context of this paper, an attractive force between the grains on either side of the intergranular phase is one that would act to thin the phase whereas a repulsive force is one that would cause the film to thicken.

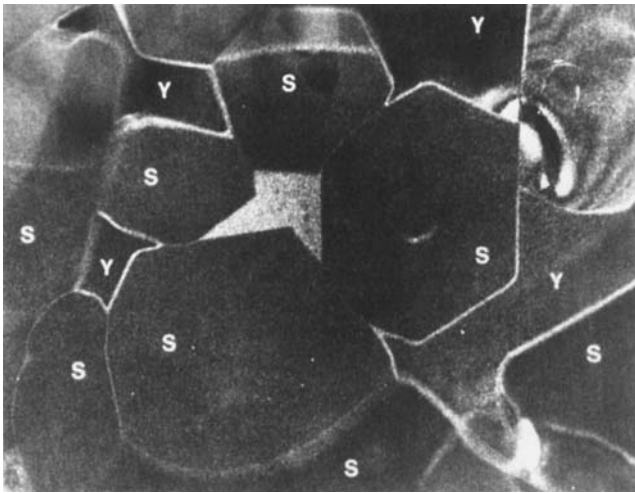


Fig. 1. Distribution of the intergranular glass phase in an yttria-alumina fluxed silicon nitride ceramic as revealed by diffuse dark field imaging in the transmission electron microscope. The micrograph, in which the intergranular phase appears bright, illustrates the characteristic difference in thickness of the intergranular phase between silicon nitride (S)-silicon nitride (S) grains and that between silicon nitride (S)-yttrium silicon oxynitride (Y) grains. (Micrograph courtesy of T. M. Shaw, and originally published in *J. Am. Ceram. Soc.*, **62** [11–12] 585–590 (1979) as Fig. 4(D).)

detected in particularly high-purity materials, such as the recent observations⁶ in Lucalox-type⁷ of alumina, where they were thought not to be present.

Perhaps the most surprising observation is that the thickness of the intergranular material (≈ 1 nm) is found to be relatively constant from one boundary to another in any given sample of material. In other words, within the accuracy of the observations, the thickness does not appear to be dependent on the angle of misorientation across the boundary, the exception being that in a number of boundaries, which are widely believed to be low-angle boundaries and boundaries of "special" orientations such as a coherent twin boundary, no intergranular phase is detectable. In polyphase ceramics, such as in many silicon nitride and sialon materials, the thickness of the intergranular phase has one value at boundaries between like phases and a different value at boundaries between dissimilar phases. An example of this is shown in Fig. 1, a micrograph of a yttria-alumina fluxed silicon nitride.⁸

Analysis of the elemental constituents of the intergranular phases in silicon nitride based materials using electron microscopy based techniques (X-ray microanalysis and electron energy loss spectroscopy) suggests that they are highly siliceous.¹⁰ Such an interpretation is consistent with the observations made by Auger electron spectroscopy of both ion-beam sputtered fracture surfaces^{11,12} and, more recently, of high-temperature in-situ fracture surfaces.¹³ Only one polyphase ceramic, a developmental nuclear waste ceramic, has been reported to contain an intergranular phase that is not siliceous and in that case it was found to be phosphate based.¹⁴ In all materials examined to date the intergranular phase is also found to contain the impurity elements and, in those cases where a sintering aid is used, the elements from the aid. In those few cases where a complete analysis has been obtained, the composition is close to that of silica. It is important to note that because of the extremely fine scale of the intergranular phase the analyses have been restricted to three- and four-grain regions rather than at the grain boundaries themselves.

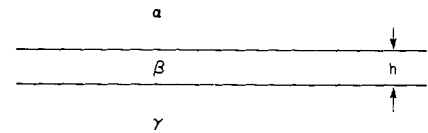


Fig. 2. Interfacial phase, β , of thickness h between phases α and γ .

III. Interfacial Energy

Consider, as the most general description of an intergranular region, the phases and geometry of Fig. 2. It is then possible to make use, as we do in this section, of established theories of interfacial free energy developed for flat interfaces between phases. In the majority of boundaries, phases α and γ will have identical properties, but as shown in Fig. 1 asymmetrical phase boundaries do also exist.

An analysis of the stability and structure of the interface between two phases, α and γ , when they are in equilibrium with an intermediate third phase, β , has been presented, within the context of the classical (van der Waals) theory of liquids, by Widom.^{7,8} Such analyses ignore the effect of long-range forces, such as van der Waals dispersion forces, as has been pointed out by Widom himself and later by de Gennes.⁹ As will be recounted in the following it is possible to show that there exists a stable, finite thickness for the β phase when the contribution of long-range van der Waals-dispersion interactions are included.

In addition to the neglect of long-range forces, the starting point of the Widom analysis is that Antonoff's rule¹⁵ for the interfacial free energies in bulk phases is satisfied:

$$\sigma = \sigma_{\alpha\beta} + \sigma_{\beta\gamma} \quad (1)$$

Provided that the β phase is in equilibrium with phases α and γ the energy of the $\alpha\gamma$ interface is a minimum when it contains a layer of β phase, irrespective of the volume fraction of the β phase (Fig. 2). As the volume fraction of the β phase is decreased, the thickness of the $\alpha\gamma$ interface continuously decreases until its thickness is of the order of a characteristic coherence length ξ . From statistical thermodynamics considerations⁷ the interface is considered to be diffuse and to have an excess free energy density over that of the bulk. For the interface, Widom⁷ expresses the difference between the free energy density in the interface and that in the bulk as a decreasing function of distance, z , measured into the bulk, to be of the form, $\exp(-|z|/\xi)$. Thus, when the thickness of the β layer at the $\alpha\gamma$ interface is of microscopic thickness, h , the excess free energy of the interface is

$$A\sigma_{\infty} \exp(-h/\xi) \quad (2)$$

where A is the interfacial area, and σ_{∞} is the interfacial energy for a bulk thickness ($h = \infty$) of the β phase.

Thus, the findings of the classical theory of liquids suggest that there is an excess free energy per unit area of interface associated with the β phase being of microscopic thickness, h , rather than of bulk thickness. In this case the net interfacial energy should be written as the sum of the interfacial energies when the phases α and γ are well separated (independent of the spacing h) plus a term describing the additional interfacial energy (which is dependent on h) when they are in relatively close proximity:

$$\sigma(h) = \sigma_{\infty}[1 + \exp(-h/\xi)] \quad (3)$$

As noted above the statistical thermodynamics approach on which the results of the previous paragraph are based neglects the effects of any long-range interactions, such as van der Waals-dispersion forces. De Gennes⁹ suggested that one way in which they can be readily incorporated is to include an additional term in the interfacial balance corresponding to the contribution of these interactions:

$$\sigma(h) = \sigma_{\infty}[1 + \exp(-3h/\xi)] + \sigma_{LRF} \quad (4)$$

⁷General Electric Co., Pittsfield, MA.

⁸The actual thicknesses measured may, in some systems, be affected by irradiation damage during observation in the electron microscope. In these cases the thickness of the intergranular phase appears to increase as a function of observation time.

where the long-range contribution is given by

$$\sigma_{LRF} = -H/12\pi h^2$$

and H is the Hamaker constant. This latter is the standard form for the van der Waals interaction energy. Mathematically, of course, it goes to $-\infty$ as the thickness h goes to zero, but this is well beyond the range of applicability sought here. The experiments (Refs. 29 to 32) in which the force between mica sheets is measured directly down to ≈ 1 nm have shown that this continuum expression is valid down to these distances.

Details of the calculation of the van der Waals contribution are given in Section IV, but the formalism of Eq. (4) is sufficient for a statement to be made on the equilibrium thickness of the β phase at the $\alpha\gamma$ interface. On differentiating Eq. (4) the thickness corresponding to the minimum interfacial energy is given by the solution to the equation

$$h^3 \exp(-h/\xi) = H\xi/6\pi\sigma_\infty \quad (5)$$

Differentiating again with respect to h indicates that the energy is a minimum, and that the system is stable, provided that $h > 3\xi$. The stable thickness may be expressed in terms of the physical parameters H , σ_∞ , and ξ , by rearranging Eq. (5) and expanding the logarithmic term:

$$h/\xi = \ln(162\pi\sigma_\infty\xi^2/H) + \ln(h/3\xi)^3 \quad (6)$$

Using the approximation $h > 3\xi$ (so that the second term on the right is always small compared to h/ξ), the stable thickness may be expressed as

$$h \approx \xi \ln(162\pi\sigma_\infty\xi^2/H) \quad (7)$$

The interfacial energy σ_∞ is itself of the order of kT/ξ^2 where k is Boltzmann's constant and T is the absolute temperature. Thus, the stable thickness of an intervening β phase at an $\alpha\gamma$ interface can be written quite generally as

$$h \approx \xi \ln(162\pi kT/H) \quad (8)$$

It should be emphasized that this approximation is a general result, based on the thermodynamics of fluids.

IV. Forces Acting on a Thin Intergranular Film

(1) Force Balance

For a stable, equilibrium intergranular phase thickness to exist it is a necessary condition that the net normal force acting on the film be equal to zero.¹⁶ This condition is satisfied by the following:

$$P + P_c + \Pi = 0 \quad (9)$$

where P is the applied pressure, P_c is the capillary pressure, and Π is the disjoining pressure. The disjoining pressure, a term originally introduced by Derjaguin,^{15,17} can usefully be considered as the net pressure due to all interfacial forces that might be acting across the intergranular liquid phase. For the most general situation the disjoining pressure consists of the contributions such as those due to (a) van der Waals forces, Π_{DISP} , (b) electrical double layer interactions, Π_{EDL} , (c) interactions resulting from solute adsorption on the two grain surfaces, Π_{ADS} , (d) hydrogen-bonding forces, Π_{HB} , and (e) any structural or steric forces, Π_{ST} . Thus, the disjoining pressure can be formally expressed as

$$\Pi = \Pi_{DISP} + \Pi_{EDL} + \Pi_{ADS} + \Pi_{HB} + \Pi_{ST} \quad (10)$$

In considering this force balance on the film in detail it is assumed that the forces are those that would act between two parallel and flat surfaces of adjacent grains across the thickness of the intergranular phase.⁸

In the absence of any experimental evidence indicating that electrical double layer interactions, solute adsorption, and hydro-

gen bonding occur in polyphase ceramics at high temperatures, it is assumed for the present purposes that their contributions can be neglected. (In passing it is noted that there is no reason to suppose that electrical double layers will not be created between crystalline grains separated by a liquid silicate at high temperatures. Likewise, solute adsorption is to be expected. In this case the contribution to the disjoining pressure is expected to be repulsive, since solute adsorption would act as an osmotic pressure.)

Subject to these simplifying assumptions, the net normal force acting across a thin intergranular phase may be written as

$$P + P_c + \Pi_{DISP} + \Pi_{ST} = 0 \quad (11)$$

(2) van der Waals-Dispersion Force

It is normally considered that the van der Waals forces between atoms or molecules can be separated into orientation, induction, and dispersion forces. Of these long-range van der Waals forces the component amenable to analysis is the dispersion force, which is conventionally referred to as the London dispersion force. This contribution has as its origin the electromagnetic interaction between fluctuating dipoles in the different phases.¹⁸ The fluctuations involved principally have frequencies in the ultraviolet region of the spectrum and are instrumental in determining the optical dispersion characteristics of the phases, hence the term dispersion forces.

When the interaction is between isolated atoms and molecules, the dispersion force is of short range and has an inverse seventh-power dependence on distance. By contrast the dispersion force interaction between solid phases is of much longer range, and varies much more slowly with distance, as Hamaker¹⁹ first showed. In a seminal paper Dzayloshinski, Lifshitz, and Pitaevski²⁰ extended the Lifshitz quantum field theory approach to the calculation of the London dispersion force to treat the case of two interacting phases separated by a third. Their result, for the parallel slab geometry of Fig. 2, can be expressed as

$$\Pi_{DISP}(h) = \frac{\hbar}{8\pi^2 h^3} \int_0^\infty \sum_{n=1}^\infty \frac{1}{n^3} \left[\left(\frac{\epsilon_\alpha - \epsilon_\beta}{\epsilon_\alpha + \epsilon_\beta} \right) \left(\frac{\epsilon_\gamma - \epsilon_\beta}{\epsilon_\gamma + \epsilon_\beta} \right) \right]^n d\zeta \quad (12)$$

where $\epsilon_j = \epsilon_j(i\zeta)$ is the dielectric permittivity of the j th phase as a function of an imaginary frequency $i\zeta$ and \hbar is Planck's constant divided by 2π .

This equation indicates that the dispersion force can be either attractive or repulsive depending on the relative values of the dielectric permittivities of the three phases. (The condition under which the dispersion force is repulsive can be stated as being when the order of the dielectric constants is changing monotonically across the boundary, i.e., $\epsilon_\alpha > \epsilon_\beta > \epsilon_\gamma$.) However, for the symmetrical case of particular interest here in which the grains on either side of the intergranular phase are the same, Eq. (12) reduces to the simpler approximate form:

$$\begin{aligned} \Pi_{DISP} &= \frac{\hbar}{8\pi^2 h^3} \int_0^\infty \left[\frac{\epsilon_\alpha(i\zeta) - \epsilon_\beta(i\zeta)}{\epsilon_\alpha(i\zeta) + \epsilon_\beta(i\zeta)} \right]^2 d\zeta \\ &= H_{\alpha\beta\alpha}/6\pi h^3 \end{aligned} \quad (13)$$

In this symmetrical case, the dispersion force will always be attractive irrespective of the nature of the materials forming the grain boundary. It is noted that this equation has the form anticipated by Hamaker.

At this point one can conclude that in the absence of an externally applied stress, P , and any capillary pressure, P_c , thin intergranular films cannot be stable against the attractive force from dispersion force interactions unless there exists a repulsive structural or steric force of sufficient strength to balance the long-range van der Waals force.

In the following section a structural model is proposed that naturally gives rise to such a repulsive force.

(3) Structural Disjoining Pressure

In the preceding sections the thickness of a stable intergranular phase has been considered in abstract, model-independent terms.

⁸The sign convention adopted here is that a positive (attractive) force is one that will act to bring the grains closer together, thereby causing the intergranular film to thin.

To proceed further and to determine the sensitivity of the thickness of the intergranular phase to experimental variables (temperature, applied pressure, capillary pressure, and grain boundary misorientation) a specific structural description of the grain boundary interfaces is required. We introduce here a structural component to the disjoining pressure. The notion of a structural disjoining pressure is not new, having been introduced by Derjaguin himself,²¹ but has not previously been given any direct physical embodiment.

It is proposed that for microscopic thicknesses of the intergranular phase the structure of the liquid phase is not random, as might be expected for bulk volumes of the phase, but rather exhibits a form of spatially varying orientational order close to each grain. If the correlation length associated with orientational fluctuations is ξ , the orientational order imposed upon the liquid-phase structure by the adjacent grains will extend a distance of the order of ξ into the intergranular phase. The orientational order is assumed to depend only on the coordinate normal to the boundary. Although it is not strictly necessary to do so, the existence of the ordering is attributed to a preference of the first monolayer of molecules of the liquid phase adjacent to each crystalline grain to adopt an epitaxial arrangement on their surfaces. (The validity of these assertions cannot presently be substantiated for the systems of interest here. However, they are not radically new in other areas of material science as explained in the Discussion section, and furthermore they are experimentally testable in principle).

In order to calculate the structural disjoining pressure, we adopt a mean field (continuum) approach in which the orientational ordering across the thickness of the boundary is expressed as a scalar quantity, $\eta(x)$. A more complete analysis would permit the order parameter as a tensor quantity, but this would preclude a tractable analysis and mask the physical insight afforded by the scalar approach. Under this set of assumptions, the free energy density of the liquid phase may be written in a Taylor series form:

$$g = g_0 + a\eta^2(x) + b\eta^3(x) + c\eta^4(x) + \dots + K[d\eta(x)/dx]^2 + \dots \quad (14)$$

This form, variously known as the Cahn-Hilliard or Landau-Ginsburg equation,^{22,23} consists of three parts. The first term, g_0 , is the free energy density in the absence of any ordering and corresponds to the free energy density of bulk, random liquid. The second part is a power series (Landau) expansion of the order parameter, η . The third part, the so-called gradient energy term, expresses the contribution due to the interaction between adjacent molecules. The symmetry of the grain boundary region, and hence the order parameter, imposes the condition that $b = 0$. It is also assumed that the constant c is small compared with a so that the term in η^4 can be neglected in comparison with that in η^2 . (This apparently arbitrary assumption is made both for reasons of tractability and because no data are available for its evaluation later. The neglect of these higher-order terms precludes the prediction of structural phase transitions of the intergranular phase, a subject beyond the scope of this initial analysis.) The excess free energy density thus reduces to the simpler form

$$g = g_0 + a\eta^2(x) + K[d\eta(x)/dx]^2 \quad (15)$$

From this expression, the excess free energy functional per unit area of boundary can be defined:

$$\Delta G = \int_{-h/2}^{h/2} (g - g_0) dx \quad (16)$$

Once a function, ΔG^{eq} , that minimizes this functional is obtained, as described in succeeding paragraphs, the structural contribution to the disjoining pressure can be calculated from the following definition:

$$\Pi_{ST} = d(\Delta G^{eq})/dh \quad (17)$$

In seeking the stable thickness of the intergranular film, it is necessary to establish the conditions under which the excess free energy functional of Eq. (16) is a minimum. The minimization procedure required is a well-posed problem in the calculus of

variations, from which it is known that the necessary conditions are satisfied by a function that is itself a solution of the Euler equation:

$$\frac{\delta g}{\delta \eta} - \frac{d}{dx} \left[\delta g / \delta \left(\frac{d\eta}{dx} \right) \right] = 0 \quad (18)$$

Such a minimum-energy solution is the following second-order differential equation:

$$\frac{d^2 \eta(x)}{dx^2} - \left(\frac{a}{K} \right) \eta(x) = 0 \quad (19)$$

whose general solution is of the form

$$\eta(x) = A \cosh (a/K)^{1/2} x + B \sinh (a/K)^{1/2} x \quad (20)$$

To proceed further it is necessary to consider specific boundary conditions. For simplicity it is assumed that the grains on either side of the boundary are misoriented such that the orientation of the first monolayers on the two grains is in opposite directions. (This case represents an upper bound on the ordering energy since this constitutes the worst conceivable misorientation of the monolayers). The boundary conditions can then be expressed as

$$\eta_0 = \eta(h/2) = -\eta(-h/2) \quad (21)$$

Applying these boundary conditions, Eq. (19) has the solution

$$\eta(x) = \eta_0 \frac{\sinh [(a/K)^{1/2} x]}{\sinh [(a/K)^{1/2} h/2]} \quad (22)$$

leading in turn to an expression for the excess free energy per unit area of

$$\Delta G^{eq} = 2(aK)^{1/2} \eta_0^2 \coth [(a/K)^{1/2} h/2] \quad (23)$$

From the definition of Eq. (17) the disjoining pressure contribution resulting from the misorientation in opposite directions is

$$\Pi_{ST} = \frac{d(\Delta G^{eq})}{dh} = - \frac{\phi_0}{\sinh^2 (h/2\xi)} \quad (24)$$

where $\phi_0 = a\eta_0^2$ and $\xi = (K/a)^{1/2}$ is a correlation length. This is a familiar form for the solution of ordering systems away from a critical point, ranging from superconductivity to order-disorder phenomena in alloys.

For the case where the thickness of the intergranular liquid phase is greater than the characteristic correlation length, i.e., for the condition $h > \xi$, the structural disjoining pressure contribution may be approximated as

$$\Pi_{ST} = -4\phi_0 \exp(-h/\xi) \quad (25)$$

The structural model thus predicts the existence of a repulsive nature (due to the negative sign) for the structural disjoining pressure as required to balance the attractive force between the grains originating from their van der Waals-dispersion interactions. It is noted that Eq. (25) has the same exponential dependence as that present in the statistical thermodynamics description of the $\alpha\gamma$ interface presented in Section III (Eq. (2)).

V. Estimate of the Equilibrium Thickness

With an expression for the structural disjoining pressure from the previous section, the net force (per unit area) acting on a thin intergranular liquid film in equilibrium can be expressed as

$$P + P_c + \frac{H_{\alpha\beta\alpha}}{6\pi h^3} - 4a\eta_0^2 \exp(-h/\xi) = 0 \quad (26)$$

In the absence of any applied and capillary stresses this equation has the same form as that presented at the end of Section III, except that it is now expressed in terms of parameters that are, in principle

²⁴As a general point, solutions to the Euler equation are extremals. To show that a particular solution is either a minimum or a maximum, the second variation must be assessed.

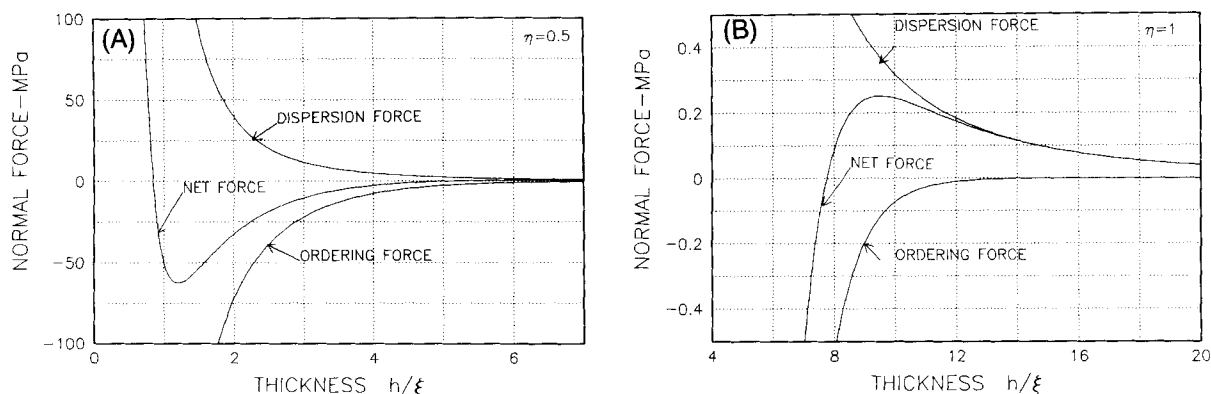


Fig. 3. Calculated contributions from the van der Waals-dispersion force and the structural disjoining pressure to the net normal force acting on a thin silica film separating alumina grains. (All forces are understood to be forces per unit area.) The thickness of the intergranular silica phase is normalized by the molecular correlation distance, ξ . The range of normal force is so large that for the purposes of illustration two regions are plotted separately, one for small spacings (A) and the other, at an expanded scale for larger spacings (B). In (A) the curves are displayed at a scale to show the general shape of the net force including the existence of a force maximum, an unstable zero force position, and the overall range of the forces. (A value of $\eta_0 = 0.5$ was used in order for the form of the equations to be visualized easily.) In (B) only the region in the vicinity of the stable zero net force position is displayed to show that region more clearly ($\eta_0 = 1.0$). At a normalized thickness of $8h/\xi$, the film is subject to a zero normal force, and the slope of the curve indicates that it is stable. The full form of the structural disjoining pressure (Eq. (24)) rather than the approximation (Eq. (25)) is graphed here.

at least, experimentally accessible. In this section Eq. (26) is evaluated leading to an approximate value for the thickness of an intergranular phase. For the purposes of illustration we consider a siliceous intergranular phase between two alumina grains, as might be found in a high-purity alumina ceramic.** In order to solve Eq. (26) we require the values of three principal parameters, the dielectric permeabilities of silica and alumina and a value for the preexponential constant, $4a\eta_0^2$.

Evaluation of the dispersion force requires, in principle, a complete knowledge of the dielectric permeabilities over all frequencies (Eq. (12)). However, as outlined in Appendix A, an accurate approximation can be computed, following the procedures described by Hough and White,²⁴ from relatively few experimental data. The required data include the principal relaxation frequencies and oscillator strengths, and in particular the optical constants. The relevant data for both silica and alumina have been determined by Hough and White and are reproduced in Appendix A. Using these data and evaluating Eq. (13) leads to a value for the nonretarded Hamaker constant for two alumina slabs separated by fused silica, $H_{\alpha\beta\alpha}$, of $5.895kT$ —a value of 1.63×10^{-19} J at 2000 K.

Evaluation of the structural disjoining pressure is also relatively straightforward. If the silica intergranular phase were fully ordered, it would correspond to crystalline silica, whereas if it were completely disordered, it would be recognized as amorphous silica. The free energy difference between these two states is a measure of the free energy of ordering and corresponds to the constant $\phi_0 = a\eta_0^2$ in Eq. (24). The appropriate numerical value to be used in quantifying this term, however, is less clear, and it is further complicated by being temperature dependent. Nevertheless, a minimum value can be assigned corresponding to the heat of melting of pure silica. Using the JANAF tables,²⁵ the heat of melting cristobalite to form silica has the value of 9.58 ± 0.2 J·mol⁻¹ (2.29 ± 0.5 kcal·mol⁻¹). This corresponds to a value of 4×10^8 Pa for the constant a .

With these values for $H_{\alpha\beta\alpha}$ and $a\eta_0^2$ the net normal force acting per unit area of an intergranular phase between two oppositely oriented grains can be written as

$$F = \frac{5.895kT}{6\pi h^3} - 1.6 \times 10^9 \eta_0^2 \exp(-h/\xi) \quad (27)$$

The structural disjoining pressure and dispersion force pressure are plotted in Fig. 3 as a function of distance normalized to the correlation length ξ . It will be noted that in the absence of capillary and applied stresses the net force acting on the intergranular film is zero at a distance of ≈ 7 to 8 correlation lengths. Assuming that the correlation length is the molecular size of the SiO₄ tetrahedral unit, i.e., ≈ 0.3 nm, then the stable thickness is ≈ 2 nm.

It will be noted that this value of the equilibrium thickness is a maximum for the alumina-silica system since complete epitaxial alignment ($\eta_0 = 1$) has been assumed in the calculation. Smaller values of η_0 lead to smaller thicknesses; for instance, a change to $\eta_0 = 0.5$ changes the predicted thickness to a value of $5\xi \approx 1.5$ nm.

From Eq. (26) the equilibrium thickness ($F = 0$) can be written explicitly as the solution of the equality

$$H_{\alpha\beta\alpha}/6\pi h^3 = 4a\eta_0^2 \exp(-h/\xi)$$

which has the same form as that predicted from interfacial energy arguments (Eq. (5) in Section III).

VI. Discussion and Implications

Two continuum approaches, one based on interfacial energies and the other on a simple force balance, indicate that a stable thickness of an intergranular liquid phase will result as a consequence of the interplay of an attractive van der Waals-dispersion interaction and a repulsive long-range structural interaction. In this respect there is a striking but predictable similarity with the findings of the DeJaguin-Landau-Verwey-Overbeek (DLVO) theory^{15,26,27} of colloid stability where a balance is sought between attractive van der Waals forces and repulsive electrostatic forces. A significant difference, however, lies in the fact that the DLVO theory is pertinent to dilute concentrations of colloids whereas in the situation considered here the particles (grains) can hardly be more crowded together.

In contrast to the well-established DLVO theory, where the origin of the repulsive force is clear, we have had to introduce a novel, structurally dependent force (which might in the terminology of polymer science be termed a steric force). By doing so we have provided one whose character is consistent with that expected from the statistical thermodynamics of polyphase liquid interfaces. This has been done on the basis of two quite reasonable assumptions, namely, the existence of some preferred epitaxial orientation of the liquid molecules on the grain surfaces imposed by the crystallographic structure of the grains themselves, and additionally the existence of a correlation between one molecule and the next adjacent one. The notion of some form of preferred

**Within the spirit of the assumptions made here, it is considered that equilibrium is established at temperatures above which intermediate phases (mullite in this case) might form.

molecular orientation on the grain surfaces is consistent with the ideas of epitaxy, long familiar in other areas of materials science. The strongest analogy is the well-documented layering and preferred orientation of the molecules of liquid crystals on substrates, even glass substrates. Such effects have not, to the author's knowledge, yet been observed for liquid silicates on ceramic surfaces. However, in the case of liquid crystal molecules on surfaces they can be readily observed.²⁸ A correlation of molecular orientations is also consistent with the polymeric view of liquid silicates, a view that silica, and incidentally water, are far from normal liquids but rather are strongly associated and exhibit many features characteristic of polymeric liquids. Having made these assumptions, the mean field theory (Eq. (14)) approach to the calculation of the structural disjoining pressure follows.

A simple way of visualizing the origin of the repulsive, structural disjoining pressure can be gained from the following thought experiment. Consider two crystalline grains having flat, parallel surfaces rotated with respect to one another and well separated by a silica liquid having a random structure. According to the assumption above, the first layer of silica molecules (SiO₄ tetrahedra) have a preferred orientation on the grain surfaces. To accommodate this alignment the silica molecules in the gap arrange themselves to match the orientation of the monolayers on either grain. When the size of the gap is large, this is a minor concern, the bulk of the silica remains liquidlike, and the distortion adds little to the overall energy of the system. The grains are now brought closer together by allowing free flow of the liquid out from the gap. As the gap gets smaller and smaller, the configurational matching becomes progressively more severe, and the silica less random. Correspondingly, the energy of the system rises. This is manifest as a force acting on the grains to resist their being brought together, a force that steadily increases in magnitude as the distortion increases as the grains are brought closer together. Clearly, when the mismatch has to be accommodated by just a few tetrahedral units, the distortion is particularly extreme, and the repulsive force correspondingly large. (In fact, when the gap is so small, it is unlikely that mere rotational distortion of silica tetrahedra will accommodate the mismatch and so may involve bond-angle distortions, in which case there will be an additional force not considered here.)

The analysis provides a ready explanation as to why the thickness of the intergranular phase is found to be of the order of 1 nm rather than tens or hundreds of nanometers. That is, the equilibrium thickness is a natural consequence of the fact that both the structural disjoining pressure and the van der Waals-dispersion force have only appreciable magnitude over distances of a few nanometers. Furthermore, the analysis indicates why the thickness of the intergranular material has a different value at boundaries between like phases and a different value at boundaries formed between dissimilar phases, as illustrated for instance in Fig. 1. In such asymmetric cases, there is still an attractive van der Waals interaction but since it is weaker the net equilibrium separation will be wider. (Since the dielectric constant of silica is generally lower than that of other ceramic phases, the condition $\epsilon_\alpha > \epsilon_\beta > \epsilon_\gamma$ is not likely to be satisfied and the dispersion interaction will hence remain attractive.) Micrographs, such as Fig. 1, clearly indicate, and perhaps contrary to expectations, that crystallographic orientation effects do not play a dominant role in determining the thickness of the intergranular material. Rather the dependence on the nature of the adjacent phases, as illustrated by the micrograph, suggest that the relative dielectric properties are determining.

It is expected that the thickness of siliceous intergranular films in ceramics other than alumina will be similar to that estimated in Section V for the particular case of a silica intergranular film between alumina grains. The structural disjoining pressure will of course be the same since it is dependent only on the nature of the silica intergranular phase. Furthermore, the Hamaker constants of most ceramics are in the range of 1 to 100 kT . However, the lack of optical constants for ceramics other than aluminum oxide and silica precludes an accurate calculation (using the formulations of Appendix A) of the Hamaker constant and hence of the equilibrium thickness of an intergranular phase. Nevertheless, an estimate (less accurate than those provided by the method of Appendix A), can

Table I. Estimated Hamaker Constants and Equilibrium Thicknesses

Ceramic system	Hamaker constant ($\times 10^{-21}$ J)	Equilibrium thickness ξ
Al ₂ O ₃ -SiO ₂ -Al ₂ O ₃	22	8.0
BeO-SiO ₂ -BeO	17	8.3
ZrO ₂ (c)-SiO ₂ -ZrO ₂ (c)	103	5.0
ZrO ₂ (t)-SiO ₂ -ZrO ₂ (t)	93	5.2
AlN-SiO ₂ -AlN	85	5.5
Si ₃ N ₄ -SiO ₂ -Si ₃ N ₄	76	5.6
SiC-SiO ₂ -SiC	233	0

be made by utilizing the Tabor-Winterton approximation²⁹ to the Hamaker constant, since this is expressed in terms of the refractive indices, n , and the dielectric constants, ϵ , of the phases; parameters known for the majority of structural ceramics. As expressed by Israelachvili,³⁰ the Tabor-Winterton approximation is

$$H_{\alpha\beta\alpha} = \frac{3}{4} kT \left(\frac{\epsilon_\alpha - \epsilon_\beta}{\epsilon_\alpha + \epsilon_\beta} \right)^2 + \frac{3\pi\hbar\nu_c}{8\sqrt{2}} \frac{(n_\alpha^2 - n_\beta^2)^2}{(n_\alpha^2 + n_\beta^2)^{3/2}} \quad (28)$$

Using values from the literature for the dielectric constants and refractive indices (collected in Appendix B), the estimated Hamaker constants for a number of ceramic systems are tabulated in Table I together with an estimate of the equilibrium thickness of a liquid silica film.

The calculated values of these systems indicate that the stable thicknesses all lie in approximately the same regime, with the exception of the silicon carbide system, where the van der Waals attraction is larger at all distances than the structural disjoining term. This is a consequence of the exceptionally high refractive index of silicon carbide. It is interesting to note that to date no silicon carbide ceramic has been observed to contain a siliceous intergranular phase.

There are a number of reasons, as mentioned in the previous sections, for the calculated thicknesses to be greater than might be observed. The first is that in Section IV(3) we have considered the geometry which has the largest possible misorientation of the adjacent grains. There are some well-defined misorientations where the structural disjoining pressure goes to zero or changes sign. In these special cases, one of which is where the adjacent grains are exactly parallel (i.e., would form a single crystal), there is no force acting to maintain a stable thickness of the intergranular phase and so it is predicted that there will be no phase present at these boundaries. Secondly, the strongest possible interaction between the grains and the first monolayer of silica tetrahedra has been assumed. This is tantamount to assuming that the tetrahedra are bound to the grain surfaces with an infinitely large binding energy. Had a finite binding force been assumed, this would have enabled (together with nonnegligible higher-order Landau constants) a theoretical exploration of possible structural phase transitions of the intergranular phase as a function of, for instance, temperature. Thirdly, the heat of melting has been attributed solely to ordering of the silica tetrahedra, which overestimates the energy of ordering. It should also be pointed out that, in practice, situations can be envisaged where the analysis does not apply and hence where the thickness of the intergranular phase will be considerably larger than that calculated here. One such case in which the analysis is inappropriate is where the grains are constrained by their neighbors from approaching sufficiently close for the interactions discussed here to operate.

The most important practical implication of this work is that if an intergranular phase wets the grain boundaries, then it will have an equilibrium thickness and cannot be removed except by (chemically) altering its interfacial energy, or by the application of extraordinarily large compressive stresses. (From Fig. 3, a compressive stress of the order of 70 MPa would be required to remove the intergranular phase when $\eta_0 = 0.5$. For the case when $\eta_0 = 1.0$ a compressive stress of 6.5 GPa would be necessary.) Application of smaller compressive stresses across the boundaries will alter the equilibrium thickness (Fig. 3(B)) but not markedly

except for these extremely high stresses. For instance, to decrease the stable thickness from $8h/\xi$ to $7h/\xi$ (a distance of only ≈ 0.3 nm) requires a compressive stress of ≈ 15 MPa. (It is important to note that application of a hydrostatic pressure alone will not be sufficient to decrease the thickness of the intergranular phase unless the liquid is free to flow from the material; i.e., the pressure applied to the grain skeleton must exceed the pore pressure in the liquid. Thus, in a hot isostatic pressing the sample must be encapsulated in a membrane permeable to the liquid phase in order to squeeze out the liquid phase.) An associated finding is that grain boundaries containing a liquid film of equilibrium thickness will be able to support a normal stress. Such a situation has not hitherto been contemplated but is expected to pertain during high-temperature deformation, for instance, under creep conditions. As presented here, the structural disjoining pressure contribution will be most pronounced in ceramics containing network-forming liquids and in liquids having strong molecular interactions (strongly associated liquids). Thus, the contribution may be especially large for silicate intergranular phases. It also suggests, as intimated above, that in the ice-water system a thin intergranular film of water will be stable at the ice grain boundaries.

It has been assumed in the foregoing that, as in sintering or hot-pressing, the boundary is subject to capillary and applied stresses trying to thin the intergranular material. During service, however, boundaries may be subject to a net tensile applied stress, i.e., one that will act so as to separate the adjacent grains. Such a condition would pertain, for instance, in the vicinity of a crack during creep rupture or generally under tensile creep. Relatively small stresses will be required to separate the grains under such conditions, since the only force that must be overcome, other than any capillary stresses, is that due to the van der Waals-dispersion interaction across the boundary. Furthermore, this becomes steadily smaller as the grains are pulled apart. From Fig. 3 the maximum tensile stress required to separate alumina grains is ≈ 0.25 MPa for the case in which $\eta_0 = 1.0$.

One consequence of the structural model introduced in Section IV(3) is that since the molecular structure of the intergranular liquid phase is nonrandom, its viscosity and diffusivity might be markedly different from those properties measured on a bulk sample of the same liquid. Of the two properties any changes in viscosity would be expected to be more detectable. Changes in diffusivity along the two-grain boundaries would be masked since in all microstructures examined to date the major fraction of the intergranular phase is located at three- and four-grain junctions. In contrast, grain boundary sliding experiments provide a measure of the viscosity of the intergranular phase, so the issue becomes whether the techniques are sensitive to any changes.

Finally, although the present paper brings considerable insight in understanding the physical origin of the thickness of intergranular thin films in ceramics, it is merely a first attempt to address the important questions as to the stability of such intergranular phases. It is also incomplete in one respect; that it is essentially a continuum description of a phenomenon taking place on a scale corresponding to atomic dimensions. As such, no attempt has been made to include the discrete nature of the solvent structure force,^{31,32} which has force minima at spacings corresponding to the size of the solvent molecule.

VII. Summary

By employing two different continuum approaches, one based on the balance of forces acting normal to an intergranular liquid film and the other on conventional diffuse interface theory, it is shown that conditions exist for intergranular phases to exhibit a stable, equilibrium thickness. Further, it is calculated that the stable thicknesses for siliceous films is of the order of only a few silica tetrahedra, ≈ 2 nm, values consistent with previously reported electron microscopy observations in many ceramics. The stable thickness is found to be strongly dependent on the dielectric properties of the adjacent grains but only weakly dependent on compressive stresses applied across the boundary. One important consequence is that, contrary to bulk behavior, a liquid inter-

granular film can withstand a normal stress.

APPENDIX A

Calculation of Hamaker Constants

In a recent review, Hough and White³³ have detailed how the results of the modern theories of dispersion forces may be implemented for the computation of Hamaker constants. The essential steps in their work are reproduced below since it provides a general procedure for calculating Hamaker constants for ceramic systems. Hough and White start by showing that the Dzyaloshinskii, Lifshitz, Pitaevskii expression (Eq. (12) in the text) for the Hamaker constant may be rewritten for computational purposes as a power series expansion:

$$H_{\alpha\beta\gamma} = \frac{3kT}{2} \sum_{n=0}^{\infty} \sum_{s=1}^{\infty} \frac{(\Delta_{\alpha\beta}\Delta_{\gamma\beta})^s}{s^3} \quad (\text{A-1})$$

where

$$\Delta_{kj} = \frac{\epsilon_k(i\xi_n) - \epsilon_j(i\xi_n)}{\epsilon_k(i\xi_n) + \epsilon_j(i\xi_n)}$$

are evaluated at frequencies

$$\xi_n = n(2\pi kT/\hbar)$$

and the prime on the summation indicates that the $n = 0$ term is given half weight. Evaluation of the function $\epsilon(i\xi)$ requires a knowledge of the absorption spectrum of the materials of interest over the entire, real frequency range. This is rarely known for many simple materials let alone ceramic materials. Therefore, the next step in the computation is the introduction of a method (the Ninham-Parsegian^{34,35} approximation) for determining this function:

$$\epsilon(i\xi) = 1 + \sum_{i=1}^N \frac{C_i}{1 + (\xi/\omega_i)^2} \quad (\text{A-2})$$

where

$$C_i = \frac{2}{\pi} \frac{f_i}{\omega_i}$$

f_i is the strength of an oscillator having a relaxation frequency of ω_i , and N is the number of oscillators.

This approximation is a method of constructing the required function $\epsilon(i\xi)$ from experimental data that are generally more available, namely, the frequencies and relative strengths of the peaks in the absorption spectrum. Particularly important is the contribution to Eq. (A-1) from the ultraviolet regions of the absorption spectrum since these are sampled in the power series many more times than the lower-frequency regions.

For the calculation of Hamaker constants of ceramic materials a further step is required since for the majority of these compounds the ultraviolet absorption peaks have not, in general, been determined. Hough and White show that the function $\epsilon(i\xi)$ can nevertheless be obtained provided that the refractive index, n , is known as a function of the wavelength in the visible region of the spectrum. Specifically, they show that a ("Cauchy") plot of the function $n^2(\omega) - 1$ against $[n^2(\omega) - 1]\omega^2$ is a straight line having a slope of $1/\omega_{uv}^2$ and an intercept of C_{uv} .

Thus, with a procedure for evaluating the ultraviolet contribution, the function $\epsilon(i\xi)$ can be constructed as

$$\epsilon(i\xi) = 1 + \frac{C_{ir}}{1 + (\xi/\omega_{ir})^2} + \frac{C_{uv}}{1 + (\xi/\omega_{uv})^2} \quad (\text{A-3})$$

The strength of the infrared contribution is given by the difference between the low-frequency dielectric constant and the square of the refractive index, viz.

$$C_{ir} = \epsilon_0 - n^2$$

and the relaxation frequency corresponds to that of the principal infrared absorption.

Table AI. Oscillator Strengths and Relaxation Frequencies

	Fused silica	Sapphire
C_{ir}	1.71	8.50
C_{uv}	1.098	2.071
$\omega_{ir} (\times 10^{14} \text{ rad} \cdot \text{s}^{-1})$	1.88	1.88
$\omega_{uv} (\times 10^{16} \text{ rad} \cdot \text{s}^{-1})$	2.033	2.017

The calculation of the Hamaker constant then reduces to the evaluation of Eq. (A-1), making use of Eq. (A-3) after the required constants are obtained from the "Cauchy" plot construction of Hough and White. For two particular ceramics, fused silica and sapphire, the oscillator strengths and relaxation frequencies required for the calculation of Hamaker constants have been determined³³ and are given in Table AI.

APPENDIX B

The refractive indices and dielectric constants used in the Tabor-Winterton approximation (Eq. (28)) to evaluate the Hamaker constants for the ceramic systems in Table I are listed in Table BI together with the literature sources from which they were obtained.

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Table BI. Refractive Indices and Dielectric Constants

Material	Refractive index	Dielectric constant
Al ₂ O ₃	1.752*	11.6 [†]
BeO	1.719 [‡]	6.7 [‡]
Fused SiO ₂	1.448*	3.81*
c-ZrO ₂ (8 mol% Y ₂ O ₃)	2.17 [¶]	38**
m-ZrO ₂	2.13 [‡]	22**
t-ZrO ₂	2.13	18 ^{††}
AlN	2.1	8.23
β -Si ₃ N ₄	2.06 [§]	8.0 [§]
SiC	2.654 ^{‡‡}	10.2 ^{‡‡}

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