Rational Design of Dispersants by Molecular Modeling for Advanced Ceramics Processing Applications†

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Abstract

A molecular modeling based approach to design-selection of dispersants for colloidal processing of ceramics powders is presented. The validity and the utility of the proposed approach are illustrated with two case studies. The relative strength of interaction of dispersants belonging to two known family of dispersants namely, hydroxy aromatics (phenol derivatives) and aliphatic/aromatic carboxylic acids with alumina are found to correlate well with the experimental trends reported in literature. The dispersibility of BaTiO₃ nanoparticles as determined by the sediment density in different organic liquids are observed to match well with the corresponding interaction energies computed theoretically.

INTRODUCTION

The benefits of very fine-grained microstructures with submicron grain sizes for obtaining ceramic components with improved hardness, wear resistance, strength or optical performance is well known [1, 2]. More recently nanocrystalline materials have been shown to possess unique physical and mechanical properties including enhanced ductility and superplasticity even in traditionally brittle materials and optical transparency in otherwise opaque ceramics [3-5]. A whole new field of nano-ceramics promises to revolutionize the industry. Rocco and Bainbridge [6] project that more than $1 trillion worth of products will be affected by nanotechnology and half of the newly designed advanced materials and manufacturing processes will be built using control at the nanoscale. Considerable progress has been made in the area of nanoparticle synthesis and processing. It is however well recognized that the conversion of these nanopowders into fully dense commercial products that retain a nanocrystalline grain size is not yet established [3, 4]. A better theoretical understanding of the fabrication processes is needed in order to manufacture high-density products without microstructural coarsening [4]. Colloidal processing methods appear to be promising in consolidating nanopowders into fully dense products [7-20].

Dispersion of colloidal particles, in particular nanoparticles in aqueous and non-aqueous suspensions is crucial for the success of manufacturing processes for advanced ceramics applications. Colloidally stable suspensions are known to produce higher average packing densities and finer pore size distributions in green/sintered compacts than poorly dispersed or flocculated suspensions [12, 21-23]. The selection of appropriate dispersants is thus important for achieving the advantages of lower sintering temperature and/or significant enhancement of performance in industrial applications, as a consequence of employing colloidal/nano particles. Commonly used dispersants include menhaden fish oil, poly vinyl butyral (PVB), phosphate esters, fatty acids & fatty acid derivatives and several varieties of polymeric dispersants [15-21, 24, 25]. Depending on the nature of the dispersant, the mechanism of dispersion could be either electrostatic, steric or electrosteric [17-22].

Design, development and selection of dispersants for different applications remain an art. Most currently available commercial dispersants are selected primarily by trial and error methods based on rules of
thumb and past experience. The time and resources required to come up with an acceptable formulation is therefore prohibitively expensive for difficult-to-disperse nanoparticles based systems. Additionally, because of the high cost of empirical search for novel dispersants, the search envelope is severely restricted to a few well-known families of dispersants. There is thus a need for devising a more cost-efficient strategy and scientifically robust framework for design/selection of dispersants in order to derive maximum advantage from using more expensive nanoparticles in industrial practice. With recent advances in the understanding of molecular level phenomena governing adsorption of dispersants at interfaces, accessibility of application oriented molecular modeling tools and availability of relatively inexpensive computing power, it is possible to design dispersants customized for specific applications that are based on theoretical computations. We have elucidated the building blocks of this novel paradigm through our recent publications on this topic [26-33]. Two key features of the proposed approach are: one, identification of the molecular recognition mechanisms underlying the adsorption of dispersants at the interface and two, use of advanced molecular modeling techniques for theoretical computations of the relative magnitude of interaction. The molecular modeling thus provides a quantitative search technique for screening and identifying the most promising molecular architectures from a large set of candidates available for a particular application. As a consequence, considerable saving in time and effort needed for developing new dispersant formulations is possible.

We present in this paper our recent work on the rational design of dispersants for colloidal processing of ceramics powders in order to illustrate the power and the utility of our molecular modeling approach. Two case studies have been selected for discussion in this communication namely, (i) the dispersion of alumina in aqueous suspensions using hydroxy aromatics (phenol derivatives) and aliphatic/aromatic specialty chemicals belonging to carboxylic acids family of reagents and (ii) the prediction of dispersion characteristics of barium titanate nanoparticles in different organic solvents. We describe very briefly the molecular modeling methodology followed by examples.

**MOLECULAR MODELLING METHODOLOGY**

**Force field calculations (Atomistic Simulations)**

Force field methods are most appropriate for relatively larger systems consisting of hundreds of atoms such as oligomers, polymers, condensed phases etc., which are of great interest in ceramics. Some of the generalized force fields currently available are Universal Force Field (UFF) [34-37], COMPASS [38] and DREIDING [39]. We have found UFF to be more suitable for the computations of the type presented in this paper. We have successfully demonstrated through our earlier work that UFF can be used to model such systems with reasonable accuracy [27-33]. The UFF is a purely diagonal and harmonic force field in which bond stretching is described by a harmonic term, angle bending by a cosine-Fourier expansion, and torsion and inversion by the cosine-Fourier expansion terms. The van der Waals interactions are modeled as Leonard-Jones potentials, and electrostatic interactions as a screened (distance-dependent) Coulombic term. All atomistic simulations in this study were carried out using the molecular modeling simulation program Cerius² [40].

**Ceramics Surface**

**Surface Energy**

The surface energy was calculated from the expression:

\[
\frac{U_s - U_b}{A}
\]

where \( U_s \) is the energy of the surface block of the crystal, \( U_b \) the energy of an equal number of atoms of the bulk crystal, and A the surface area.

**Alumina (001) Surface**

The Al-terminated (001) basal plane of \( \alpha \)-alumina (corundum) has been found to be energetically most stable [21]. The hexagonal unit cell was cleaved at (001) plane to create an eighteen atomic layer thick surface cell. This surface cell was replicated in x and y planes to create a super cell of 21.22×21.22 Å. While relaxing the surface, top nine atomic layers were allowed to move and rest of the nine layers were constrained. The calculated surface energy (1.37 J/m²) was comparable to reported values (2.42 J/m²) [41].

**Barium Titanate (001) Surface**

We have recently reported [33] our work on molecular modeling of dispersion of nanoparticles of barium titanate using a variety of commercial dispersants including fatty acids and phosphate esters. The systematic force field and ab initio calculations were performed to arrive at the most stable BaTiO₃ surface. Based on the surface energies, BaO terminated (001) surface 0.83 J/m² was found to be more relaxed com-
pared to TiO$_2$ terminated (001) surface 2.65 J/m$^2$. The surface thus obtained was converted into a three dimensional periodic structure by adding a vacuum of 50 Å in Z-direction. This computer representation of BaTiO$_3$ was used in the present study as well.

Dispersant Molecules

Three family of dispersants namely, aromatic alcohols, aromatic carboxylic acids and aliphatic carboxylic acids were selected for the study. The molecules were optimized using UFF method.

Ceramics-Dispersant Complex (in vacuum)

The optimized dispersant molecule was docked on the ceramics surface. The initial geometry of ceramics-dispersant complex was created physically on the screen with the help of molecular graphics tools, taking into consideration the possible interactions of dispersant functional groups with surface atoms. The dispersant molecule was then allowed to relax completely on the surface. Several initial conformations (~20) were assessed so as to locate the minimum energy conformation of dispersant molecule at the ceramics surface.

Static Energy Minimization (Simulation Details)

The partial charges on the atoms were calculated using charge equilibration method [42]. The intramolecular van der Waal interactions were calculated only between atoms which are located at distances greater than fourth nearest neighbors. A modified Ewald summation method [43] was used for calculating the non-bonded coulomb interactions while for van der Waal interactions atom based direct cut off method was employed. Smart minimizer as implemented in Cerius$^2$ was used for geometry optimization. The optimization was considered to be converged when a gradient of 0.0001 Kcal/mole is reached.

Solvent Box

A three dimensional periodic box of solvent molecules was constructed and optimized so as to match the density in the box to that of the experimental density of the selected solvent. NVE molecular dynamics (MD) simulations were run for 300 ps to equilibrate the solvent box at 300 K at its experimental density.

Ceramics Surface – Dispersing Medium

Bulk solvent molecules, equilibrated as described in the previous section, were introduced over the ceramics surface. The ceramics surface-solvent complexes thus created were subjected to energy minimization and molecular dynamics simulation.

Molecular Dynamics (MD) Simulations (in presence of solvent)

Structure of the complex obtained through static energy minimization method represents only a local minimum energy structure, which was used as initial configuration to find a global minimum energy structure through molecular dynamics (MD) simulations. MD calculations were run using constant energy microcanonical ensemble method (NVE) at 300 K with time step of 1 fs. Total run length was ~100 ps. During the simulations, the temperature was controlled by velocity scaling method. During simulations, atom-based cut-off method was employed for calculating both Van der waals and electrostatic forces. A typical optimized ceramic surface – dispersant complex in presence of the solvent is shown in Figure 1.

Computation of Interaction Energy

The relative affinity of interaction of different dispersants with ceramics surface in presence or absence of the solvent can be quantified in terms of the interaction energy defined as follows:

In vacuum, (absence of dispersing medium):
The authors defined a dispersibility index in percent based on sediment volume measurements. Higher the value of this index the better is the dispersion. The theoretical predictions match well with the experimental findings.

**Aqueous alumina suspensions**

Hideber et al. [45] studied the relation between the molecular structure of low-molecular weight organic dispersants namely, hydroxy aromatics and aliphatic/

\[
IE_{\text{in vacuum}} = E_{\text{complex,vacuum}} \cdot \Sigma (E_{\text{surface}} + E_{\text{dispersant}}) \quad (1)
\]

In the presence of dispersing medium:

\[
IE_{\text{in solvent}} = \Delta E_{\text{combined}} \cdot \Sigma (\Delta E_{\text{solvent-dispersant}} + \Delta E_{\text{surface-solvent}}) \quad (2)
\]

\[
\Delta E_{\text{combined}} = E_{\text{complex,solvent}} \cdot \Sigma (E_{\text{surface}} + E_{\text{dispersant}} + E_{\text{solvent}}) \quad (3)
\]

where \(\Delta E_{\text{combined}}\) is the total interaction energy calculated using Eqn. 3. \(E_{\text{complex,solvent}}\) is the total energy of the optimized surface-dispersant complex in the presence of solvent, \(E_{\text{surface}}\), \(E_{\text{dispersant}}\) and \(E_{\text{solvent}}\) are the total energies of free surface, dispersant and solvent molecules, computed separately. \(\Delta E_{\text{solvent-dispersant}}\) is the interaction energy computed for the interaction of solvent and dispersant molecules and \(\Delta E_{\text{surface-solvent}}\) is the contribution due to interaction of solvent molecules with the surface. These energies are subtracted from \(\Delta E_{\text{combined}}\) to get the final interaction energy \([IE_{\text{in solvent}}]\) of dispersant molecule with the ceramic surface (Eqn. 2).

It is worth noting that the more negative magnitude of interaction energy indicates more favorable interactions between the dispersant and surface. The magnitude of this quantity is thus an excellent measure of the relative intensity/efficiency of interaction amongst various dispersants.

**RESULTS AND DISCUSSIONS**

**BaTiO\(_3\)** dispersions in organic media

Mizuta et al. [44] studied the fundamental properties of BaTiO\(_3\) dispersions in pure organic liquids including alcohols, aldehydes, acids, ketones, hydrocarbons and water by sediment volume and contact angle measurements using four different powders namely, TAM-C, TAM-COF, Transelco (219-3) and Fuji BT-100PL. The experimental trends with respect to wettability and dispersion were found to be similar for all the four powders. We have taken the data for a typical powder, Fuji BT-100PL for comparing with our theoretical findings. Benzaldehyde was found to be the best dispersing medium. Based on their experimental work, the authors inferred that the intensity of interactions between organic functional groups and BaTiO\(_3\) surface was as follows:

Acid = aldehyde

= alcohol > ester > ketone > ether > hydrocarbon

We have calculated interaction energies for some of the solvents with BaTiO\(_3\) surface. Our results are compared with experimental results of Mizuta et al.
aromatic carboxylic acid and their influence on the dispersion behavior of alumina suspensions. In particular, the effect of the nature, number and position of the functional groups attached to the benzene ring were studied through adsorption and electrophoretic mobility experiments on aqueous alumina suspensions. The amount adsorbed was calculated from the difference between the amount of dispersant added and that remaining in the supernatant. The results were plotted in terms of adsorption as percent of the amount added. The initial concentration was maintained at $10^{-3}$ mole per litre.

The degree of adsorption (that is, the efficiency) of a dispersant increased with its ability to form one or more chelate rings with the ceramic surface. It also increased with increasing number of functional groups in a homologous series.

We have modeled the interactions of these dispersants with alumina surface. Our theoretical findings are compared with experimental results in Figures 3, 4 and 5.

**Aromatic Alcohols**

Computed interaction energies of phenol, catechol and pyrogallol with alumina are plotted and compared with experimental percent adsorption in Fig. 3. The predicted trends match well with experimental findings. As expected, the interaction energy becomes more negative with increasing number of -OH groups in the dispersant molecule.

**Aromatic Carboxylic acids**

The calculated interaction energies of benzoic, phthalic and hemimellitic acids with alumina are plotted in Fig. 4b. The corresponding experimental adsorption data compares well with the theoretical findings (Fig. 4a). The interaction energy is most favorable for the molecule with the highest number of functional groups in the benzene ring.

**Aliphatic Carboxylic Acids**

As shown in Fig. 5a the adsorption of propionic acid is lowest (only one carboxylic group). The presence of a hydroxyl group in $\alpha$-position (lactic acid) enhances the adsorption. The adsorption at alumina surface increases with increasing number of functional groups: citric acid (three carboxyl) > malic acid (two carboxyl) > lactic acid (one carboxyl with $\alpha$-hydroxyl) > propionic acid (one carboxyl). Based on the computed interaction energies, predicted order of adsorption was found to be: citric acid > malic acid > lactic acid > propionic acid (Fig. 5b).
Fig. 4  (a) Adsorption curves for aromatic carboxylic acids on $\alpha$-alumina (data taken from Ref. [45]), (b) Theoretically computed interaction energies obtained using MD simulations in presence of water.

Fig. 5  (a) Adsorption curves for aliphatic carboxylic acids on $\alpha$-alumina (data taken from Ref. [45]), (b) Theoretically computed interaction energies obtained using MD simulations in presence of water.
CONCLUDING REMARKS

The utility of currently available molecular modeling tools in the design and screening of different molecular architectures for dispersion of ceramic powders is demonstrated through this communication. The relative efficiency of specialty chemicals for a particular ceramic powder-solvent system can thus be theoretically predicted. The molecular modeling based theoretical approach thus provides a scientifically theoretically predicted. The molecular modeling based particular ceramic powder-solvent system can thus be the desired application.

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**Author’s short biography**

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Pradip, currently the Group Leader, Materials and Minerals Processing Technology Group at Tata Research Development & Design Centre (TRDDC), Pune, received his B.Tech in Metallurgical Engineering from IIT, Kanpur in 1975 and M.S. and Ph.D. in Materials Science and Mineral Engineering from University of California at Berkeley in 1977 and 1981 respectively. He also spent three years as a scientific officer at Bhabha Atomic Research Centre (BARC) before joining TRDDC in 1984. His main areas of research include particle science & technology, mineral processing, design and development of performance chemicals based on molecular modeling, applied surface and colloid chemistry, mathematical modeling & simulation of particulate processing systems, colloidal processing of advanced ceramics, waste recycling and cement chemistry.

With more than 120 publications and eight patents to his credit, Pradip is the recipient of several honors including National Metallurgist Award, Kuczynski Prize of IISS. Pradip is Fellow, Indian National Academy of Engineering (FNAE) and Fellow, Institute of Materials (FIMMM), UK. He is associate editor of International Journal of Mineral Processing, Bulletin of Materials Science and Transactions, Indian Institute of Metals. He has edited several special issues of international journals, the latest being the Special Issue of Ferroelectrics on Selected Topics in Advanced Materials Research (2004).

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