SURFACE PHENOMENA

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Summary

Many food systems are dispersed systems in which one phase is dispersed into a second immiscible phase in the form of fine particles or droplets. When the two phases are liquids, the product is an emulsion. When one phase is air, the product is foam, in which the air bubbles are separated by thin aqueous films. Because of the large free energy associated with the large interfacial area, such systems are thermodynamically unstable. The shelf life of such products are prolonged by providing kinetic stability through the use of proteins and emulsifiers that modify the surface, as well as interaction forces between dispersed particles through the formation of an adsorbed interfacial layer. The evaluation of colloidal van der Waals, electrostatic, and steric interactions is discussed.

Calculation of the rate of flocculation of dispersed particles due to Brownian and gravitational motion is presented. Characterization of surface activity of small molecular weight surfactants via hydrophile-lipophile balance and the Gibbs adsorption equation is discussed. Lattice models for prediction of the adsorption isotherm of proteins at fluid-fluid interfaces are presented and compared with experimental data for some model protein systems. Energy barriers for adsorption of proteins at fluid-fluid interfaces are discussed. Models for the kinetics of protein adsorption accounting for these energy barriers in terms of molecular properties of proteins are presented and their predictions compared with experimental data. Finally, competitive adsorption of mixed emulsifier-protein systems at fluid-fluid interfaces and its effect on interfacial rheological properties are discussed.

1. Introduction

In many food products such as mayonnaise, whipped cream butter, and sauces, one phase (air, water, oil, or solid particles) is dispersed in the other phase. When the two phases are liquids, the product is called an emulsion, which is further sub-classified as oil-in-water or water-in-oil emulsion, depending on the nature of the dispersed phase (see *Food Emulsions*). Milk and mayonnaise are examples of oil-in-water emulsions, whereas butter is a water-in-oil emulsion. When the dispersed phase is air, the product is called foam. Ice cream and whipped cream are good examples of foam. When the dispersed phase is solid particles, the product is known as a dispersion (see *Food Suspensions*). Different types of sauces are examples of dispersions. Of course, many of these products are indeed combinations of emulsions, foams, or dispersions. Since one phase is dispersed in the form of very fine particles over a large interfacial area, such dispersions are thermodynamically unstable, i.e., eventually the system will phase separate. Phase separation occurs as a result of flocculation, followed by coalescence of colliding particles (see *Separation*). Particle collision in such colloidal systems is brought about by either thermal motion or gravitational motion caused by the density difference between the dispersed and continuous phases. The gravitational motion leads to creaming, thus resulting in the formation of a cream layer in the case of emulsion, which subsequently leads to coalescence and phase separation. In order to provide kinetic stability to these colloidal systems, with desirable shelf life, food emulsifiers are added. Food emulsifiers can be either small molecular weight surfactants such as monoglyceride or macromolecules such as proteins. By virtue of their surface activity, food emulsifiers adsorb at air-water, oil-water, or solid-water interfaces. Enhancement of shelf life is brought about by several mechanisms, namely, 1) the modification of interaction between dispersed particles by providing repulsive interactions, thereby preventing or slowing down flocculation or coalescence of colliding particles and 2) the modification of interfacial rheological properties in the case of emulsions and foams, thereby slowing down the drainage of the continuous phase between two colliding dispersed particles. In addition to providing shelf life, food emulsifiers also facilitate the formation of foams and emulsions of sufficiently small particles by reducing the surface/interfacial tensions due to their surface activity. Of course, the efficacy of food emulsifiers will depend on their surface activity. This chapter briefly describes the interaction between dispersed particles, the interfacial behavior of food emulsifiers and proteins, and their effect on the long-term stability of dispersed food systems.

2. Colloidal Forces Between Particles

As pointed out above, an important factor affecting the stability of a colloidal dispersion is the nature of the interparticle forces. The dispersed particles always experience van der Waals attractive forces. In addition, adsorption of proteins and ionic surfactant will impart charge to the colloidal particles, thereby introducing electrostatic repulsive forces between them. The adsorption of proteins will also introduce steric interactions. To better understand the role of food emulsifiers on colloidal stability, it is important to quantify these interactions.

2.1. Van der Waals Interaction

Van der Waals interaction is the result of permanent dipole-permanent dipole, permanent dipole-induced dipole, and induced dipole-induced dipole interactions between molecules. Of these, induced dipole-induced dipole interactions, known as dispersion forces, are experienced by all molecules and have their origin in the rapidly fluctuating dipole moment of a neutral molecule, which polarizes other neighboring molecules, thus giving rise to attractive interactions. Assuming pairwise additivity, the van der Waals interactions U_{vw} between two spherical particles for distances of separation much smaller than the particle radii is given by:

$$U_{vw} = -\frac{AR_1R_2}{6h(R_1 + R_2)} \qquad R_1, R_2 >> h \tag{1}$$

where R_1 and R_2 are the radii of both particles, A is the effective hamaker constant, which depends on the polarizabilities, and h is the surface to surface distance between the two particles. Van der Waals attraction is a fairly, long-range interaction, with the attractive force increasing significantly at shorter distances of separation. When the distance of separation between the particles is on the order of wavelength of electromagnetic radiation (typically in the order of 100 nm), dipoles shift during the propagation, causing retardation effects, which diminish the attraction and therefore cannot be neglected. Simplification of expressions for the retardation can be found elsewhere.

For particles (2) dispersed in a continuous medium (1), the effective Hamaker constant A_{212} is given by:

$$A_{212} = (A_{11}^{1/2} - A_{22}^{1/2})^2 \tag{2}$$

The effective hamaker constant is very sensitive to the polarizability of the medium. The net force is always attractive, becoming zero only when the dispersed and the continuous phases have the same polarizability. Generally, the adsorbed layer of proteins tends to decrease the net van der Waals attraction, the extent of reduction being dependent on the nature and the thickness of the adsorbed layer.

2.2. Electrostatic Interactions

Adsorption of ionic proteins and surfactants imparts charge to the colloidal particles. Electroneutrality requires that the net particle charge be counterbalanced by preferential accumulation of oppositely-charged counterions in the vicinity of the charged surface. Because of thermal motion, the neutralization occurs over a region known as the electrical double layer. The double layer consists of an inner compact stern layer and an outer diffuse layer. The electrostatic potential profile within an electrical double layer can be obtained by solving the Poisson-Boltzmann equation. The thickness of the electrical double layer depends on the ionic strength of the continuous medium, the valence number of the counterion, and the dielectric constant of the medium, given by:

$$\kappa = \left(\frac{2000 e^2 N_A I}{\varepsilon_0 \varepsilon_r kT} \right)^{1/2} \tag{3}$$

where κ, the Debye-Huckel parameter, is inversely proportional to the double layer thickness, ε_0 is the permittivity of vacuum, ε_r the dielectric constant of the medium, e the elementary charge, N_A the Avagadro number, k the Boltzmann constant, T the temperature, and the ionic strength I is given by:

$$I = \frac{1}{2} \sum_{i=1,2} z_i^2 M_i \tag{4}$$

where z_i is the valence number of i^{th} type of ion and M_i is the molar concentration of i^{th} type of ion in the bulk. The double layer thickness decreases with increase in the ionic strength as well as with the valence number of the counterion.

When two colloidal particles approach each other, they experience a force of repulsion because of the overlap of double layers that surrounds each particle. This repulsion is due to the difference in the electrostatic potential profile in the overlap region compared to an isolated double layer, thus resulting in a net repulsive interaction. The interaction can be calculated from the electrostatic potential profile obtained from the solution of the Poisson Boltzmann equation in the region between the two particles. The relative motion between the two colliding particles is relatively slow, thus the surface potential of the approaching particles is usually assumed as constant. When the double layer around each particle is sufficiently thin, (i.e., κR is sufficiently large), Derjaguin's procedure can be employed to evaluate the interaction between two spherical particles using the results of interaction between two charged plates. For low surface potentials, the interaction potential between two equal-sized particles of radius R is given by:

$$U_{el} = 2\pi \varepsilon_0 \varepsilon_r R \psi_0^2 \ln\{1 + \exp(-\kappa h)\} \tag{5}$$

where ψ_0 is the surface potential of the particle. When the surface potential is not low, the electrostatic interaction potential can be evaluated for negligible overlap of the two double layers, yielding:

$$U_{el} = \frac{64 n_0 kT \gamma_0^2}{\kappa} \exp(-\kappa h) \tag{6}$$

where n_0 is the bulk number concentration of electrolyte and γ_0 is related to the surface potential via

$$\gamma_0 = \frac{\exp(\frac{ze\psi_0}{2kT}) - 1}{\exp(\frac{ze\psi_0}{2kT}) + 1} \tag{7}$$

The surface potential ψ_0 is usually taken to be the zeta potential, the potential at the plane of shear.

2.3. Steric Interaction

2.3.1. Forces Due to Adsorbed Macromolecules

When proteins are employed to provide stability to emulsions, foams and colloidal dispersions, they adsorb at the interface and form a thick, adsorbed layer. The adsorption characteristics of proteins at the interfaces will be discussed in detail later in the following sections. When two colloidal particles with adsorbed protein layers approach each other, the overlap of the adsorbed layer usually results in a steric repulsive interaction between the two particles. If the surface-to-surface distance of separation between the two particles is greater than twice the thickness of the adsorbed layer, the two particles will not experience any steric interaction, since the adsorbed layers do not overlap. If the surface-to-surface distance of separation is between one and two spans of the adsorbed layer, i.e., $L_s \le h \le 2L_s$, L_s is the thickness of the adsorbed layer, the adsorbed segments will overlap but will not be compressed. In this regime, the steric interaction between the two particles is due to the difference in the free energy of mixing between the adsorbed segments and the solvent in the overlap region, because of the increase in the segment density. Whenever the interaction between the segments and the solvent is favorable, i.e., the solvent is good, the overlap of the adsorbed layers results in an increase of free energy, which manifests itself as a steric repulsion. Proteins generally have a favorable interaction with water (solvent). As a result, steric repulsion is usually experienced by the colloidal particles stabilized by proteins. For uniform segment density of proteins in the adsorbed layer, the steric interaction U_{steric} between two spherical particles of radii R is given by:

$$U_{steric} = 4\pi R \omega^2 N_A (\frac{\bar{v}_2^2}{\bar{v}_1})(\frac{1}{2} - \chi) kT (1 - \frac{h}{2L_s})^2 \tag{8}$$

where ω is the weight of the adsorbed segments per unit area, χ is the Flory Huggins parameter, $\bar{v}_1$ is the molar volume of the solvent, and $\bar{v}_2$ is the partial specific volume

of protein. Since the interaction between protein and the solvent is usually favorable, $\chi < \frac{1}{2}$. As a result, $U_{steric} > 0$, i.e., steric interaction is repulsive.

When the minimum surface-to-surface distance of separation between two particles is less than the thickness of the adsorbed layer, (i.e., $h \le L_s$), loops and tails of adsorbed protein segments are compressed by the other particle. This compression always results in a repulsive interaction irrespective of the nature of the solvent, since loss of configurations due to compression leads to a decrease in entropy and therefore an increase in the free energy. For constant segment density in the adsorbed layer, the steric interaction is given by:

$$U_{steric} = 4\pi R\omega^2 N_A \left(\frac{\bar{v}_2^2}{\bar{v}_1}\right)\left(\frac{1}{2} - \chi\right)kT \{\ln\left(\frac{L_s}{h}\right) - \frac{1}{4} + \frac{h}{2L_s}\} + 2\pi RkT\nu L_s\left(1 - \frac{h}{L_s}\right)^2 \quad (9)$$

where ν is the number of adsorbed segments per unit area. It should be noted that the second term is the elastic contribution to the interaction energy, which arises from the compression of the adsorbed segments.

2.3.2. Forces Due to Free Macromolecules

Water soluble polymers such as gums, pectins, and gelatin can cause flocculation when present at very low concentrations. When the distance of separation between two colloidal particles becomes comparable to the radius of gyration of the water soluble polymer, the free energy of the macromolecule in the region between the two particles will increase because of geometric constraints. As a result, the two particles experience a repulsive interaction. If the two particles are able to overcome this energy barrier and come closer, then the water soluble polymer is completely excluded in the region between the particles, since the distance of separation is now much smaller than the radius of gyration. Consequently, the osmotic pressure of the polymer solution does not act on the particles in the region between them, thus resulting in an attraction between particles. The attractive interaction between two particles is given by:

$$U_{steric} = -\pi_{osmotic}(\pi/12)\{2(2R + R_g)^3 - 3(2R + R_g)^2(2R + h) + (2R + h)^3\} \quad (10)$$

where the osmotic pressure $\pi_{osmotic}$ can be related to the polymer number concentration n_{pol} via:

$$\pi_{osmotic} = kTn_{pol} \quad (11)$$

2.4. Combination of Forces

The combination of different interparticle forces discussed above determines the stability of colloidal dispersion to flocculation. The dispersion can be classified as 1) unstable, 2) metastable, and 3) stable. In an unstable dispersion, the net interaction is attractive except at very short distances of separation with the net interaction potential exhibiting a potential well where flocculation can occur. This happens when the repulsion is either small or short ranged. In a metastable dispersion, van der Waals attraction is dominant at very small and large distances, whereas repulsion is predominant at intermediate distances of separation, resulting in an energy barrier as shown in Figure 1. This is usually the case for electrostatically stabilized systems. In a stable system, repulsion predominates over van der Waals attraction for the entire range of separation distance. This is typical of a sterically stabilized system.

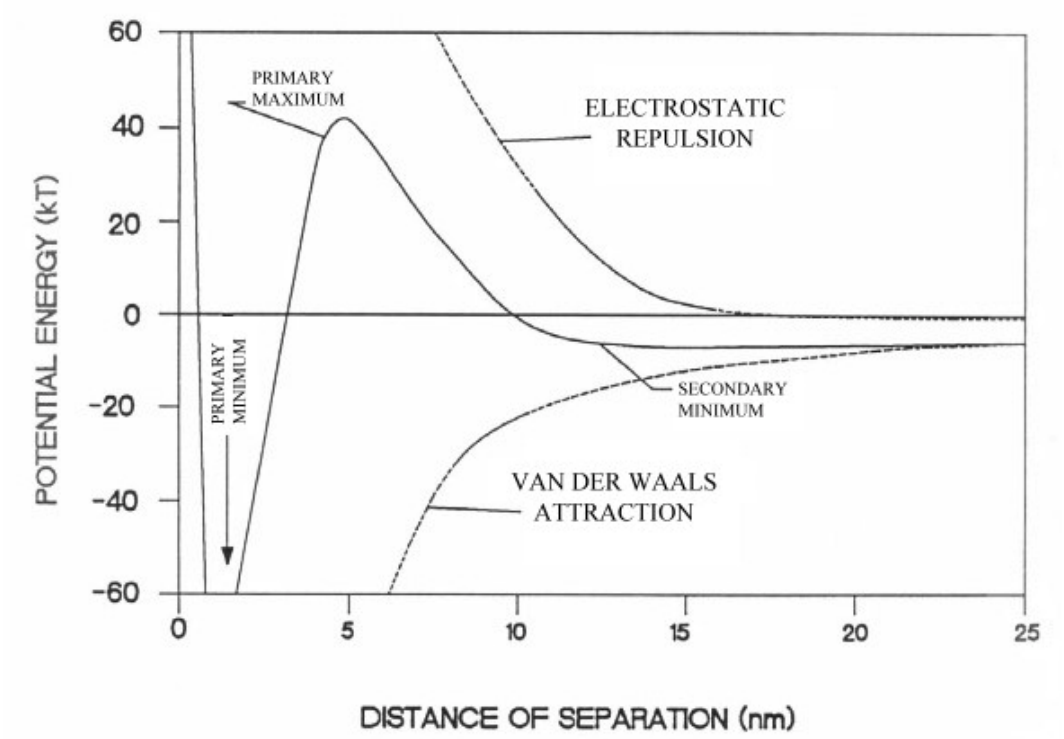

Figure 1. Potential energy versus distance for a pair of electrostatically stabilized particles. The separate contributions of van der Waals and electrostatic interactions are also shown.
[From: Narsimhan G. (1992). Emulsions, in *Physical Chemistry of Foods* (eds. H.G. Schwartzberg and R.W. Hartel). New York: Marcel Dekker].

3. Flocculation

In an unstable or a metastable system, van der Waals attraction leads to flocculation of a colliding pair of particles when the distance of separation between the two particles is small. Flocculation can be considered as a precursor to coalescence, and therefore it is important to know the rates of flocculation. The three mechanisms of particle loss are Brownian flocculation, gravitational flocculation, and creaming.

3.1. Brownian Flocculation

Brownian flocculation occurs because of a collision between the particles due to thermal motion. The effect of interparticle forces on Brownian flocculation is accounted for in the following expression for the rate of slow flocculation:

$$J_s = \frac{8\pi RDn_0}{W} \tag{12}$$

where D is the diffusion coefficient of the particle, n_0 is the particle number concentration, and the stability ratio W is given by:

$$W = 2R\int_{2R}^{\infty} \exp(\frac{U_{total}}{kT})\frac{dr}{r^2} \tag{13}$$

In the above equation, U_{total} is the sum of different interaction potentials between the two colliding particles. In the absence of interparticle forces, the stability ratio is unity. Consequently, the numerator in Equation (12) gives the fast flocculation rate. Reerink and Overbeek (1954) have evaluated the following approximate expression for the stability ratio:

$$\log W = A - B\frac{R\gamma_0^2}{z^2}\log c \tag{14}$$

where A and B are constants, c is the electrolyte concentration, and z the valence number of the electrolyte. Equation (14) predicts that a log plot of W vs. c should yield a straight line in the slow flocculation regime. One can also identify a critical flocculation concentration of the electrolyte at which the stability ratio becomes unity. For electrolyte concentrations greater than the critical flocculation concentration, the stability ratio will still be unity because of the absence of an energy barrier. Consequently, a plot of $\log W$ vs. $\log c$ should consist of two straight lines intersecting at the critical flocculation concentration. The critical flocculation concentration has been shown to vary as the inverse sixth power (z^{-6}) of the valence number of the electrolyte for symmetrical electrolytes, such as NaCl, for example. In the case of non-symmetrical electrolytes, the valence number of the counterion has been found to influence the critical flocculation concentration.

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Haynes C.A. and Norde W. (1994). Globular Proteins at Solid/Liquid Interfaces. *Colloids and Surfaces B: Biointerfaces* **2**, 517. [This review presents different factors that influence protein conformation in solution and protein adsorption at solid interfaces. Factors affecting protein folding and stability are discussed. Data on molecular dimensions and hydrophobicities of a variety of globular protein are given. The influences of protein hydrophobicity, charge, sorbent polarity, protein structural stability on adsorption isotherm of some globular proteins are presented. Hydrogen ion titration curves of some globular proteins are also presented. Thermodynamics of protein adsorption and principle forces involved in protein adsorption at solid interfaces are discussed].

Hiemenz P.C. and Rajagopalan R. (1997). *Principles of Colloid and Surface Chemistry*, Third Edition. New York: Marcel-Dekker. [This book on colloid and surface chemistry gives an excellent introduction to interparticle forces, electrical double layer, electrostatic and polymer-induced colloid stability, surface tension, Gibbs adsorption equation, osmotic and donnon equilibria, etc.].

Hunt J.A., Dickinson E., and Horne D.S. (1993). Competitive Displacement of Proteins in Oil-in-Water Emulsions Containing Calcium Ions. *Colloids Surf. A:* **71**, 197 [In the absence of calcium ions, addition of β casein to a phosvitin stabilized oil-in-water emulsion results in 70 percent of the originally adsorbed phosvitin becoming displaced within a few minutes, followed by the loss of a further 10 percent over a 48 hour period. In contrast, when calcium ions are present at a concentration sufficient to cause droplet aggregation in a mixed emulsion, no phosvitin is desorbed, despite substantial adsorption of the added protein. Displacement of phosvitin is facilitated when sufficient calcium ions are present to cause aggregation].

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Murray B.S. and Dickinson E. (1996). Interfacial Rheology and the Dynamic Properties of Adsorbed Films of Food Proteins and Surfactants. *Food Sci. Technol. Int.* (Jpn) **2**, 131. [Factors affecting the interfacial rheology of films of food proteins and surfactants at air-water and oil-water interfaces are reviewed. A comparison is made between properties of adsorbed layers of small-molecule surfactants, proteins and mixed systems of protein+surfactant. The relationship between interfacial rheology and stability of emulsions is discussed].

Napper D.H. (1983). *Polymeric Stabilization of Colloidal Dispersions*. Academic Press, New York. [This book is a comprehensive treatment of different aspects of polymeric stabilization of colloidal dispersions. It introduces polymer solution thermodynamics and conformation of polymer molecules in solution and builds upon it to describe steric interaction between surfaces with attached polymers. It discusses theories of polymer stabilization and experimental data on colloid stability as well as distance dependence of steric interactions. Theoretical and experimental aspects of depletion flocculation and stabilization are also included].

Narsimhan G. and Uraizee F. (1992). Kinetics of Adsorption of Globular Protein at an Air-Water Interface. *Biotechnol. Prog.* **8**, 187. [Adsorption of globular proteins at an air-water interface from an infinite stagnant medium was modeled as one-dimensional diffusion in a potential field. The interaction potential experienced by an adsorbing protein molecule consisted of contributions made from electrostatic interactions, work done against the surface pressure to clear area at the interface in order to anchor the adsorbed segments, and the change in free energy due to exposure of penetrated surface hydrophobic functional groups to air. The energy barrier to adsorption, present at larger surface pressures, was found to be higher for smaller surface hydrophobicities, larger surface pressures, larger size molecules, and oblate orientation of an ellipsoidal molecule. More adsorption was shown to occur at larger surface hydrophobicities, smaller size molecules, and for prolate orientation of ellipsoidal molecules. The model predictions agreed with the experimental data for lysozyme].

Narsimhan G. (1992). Emulsions, in *Physical Chemistry of Foods* (eds. H.G. Schwartzberg, and R.W Hartel). New York: Marcel Dekker. [This book chapter elucidates the role of proteins and emulsfiers in the stabilization of food emulsions. It describes the colloidal forces between particles. Flocculation of droplets due to creaming and Brownian motion are described. The role of thin film drainage and stability on drop coalescence is discussed. A brief discussion of drop break-up in a turbulent flow field during emulsion formation is also included].

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interfaces, competitive adsorption of mixed emulsfiers, and break-up of droplets during emulsion formation].

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Schenkel J.H. and Kitchener J.A. (1960). A Test of the Derjaguin-Verwey-Overbeek Theory with a Colloidal Suspensions. *Trans. Faraday Soc*. **56**, 161. [Validation of DLVO theory of colloid stability from experimental data of evolution of particle number concentration from a coagulating colloidal suspension].

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Uraizee F. and Narsimhan G. (1991). A Surface Equation of State for Globular Proteins at the Air-Water Interface. *J. Colloid Interface Sci*. **146**, 169. [A lattice model for surface equation of state of globular proteins at air-water interface was proposed accounting for the structure of the protein molecule, its degree of unfolding, segment-segment, segment-solvent, and electrostatic interactions. Fitting the equation to the experimental data indicates that the average degree of unfolding of BSA is greater than that for lysozyme. The number of adsorbed segments for BSA was found to vary linearly with the surface concentration, whereas the adsorbed segments for lysozyme were fairly independent of surface concentration. Due to exposure of unfolded hydrophobic functional groups, segment-solvent interactions were found to be unfavorable].

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Wüstneck R., Krägel J., Miller R., Fainerman V.B., Wilde P.J., Sarker D.K., and Clark D.C. (1996). Dynamic Surface Tension and Adsorption Properties of β casein and β Lactoglobulin. *Food Hydrocolloids* **10 (4)**, 395. [The adsorption kinetic behavior of β lactoglobulin and β casein solutions studied by dynamic surface tension measurements was interpreted by diffusion controlled models].

Biographical Sketch

Ganesan Narsimhan is a Professor of Agricultural & Biological Engineering at Purdue University. His monograph "*Surface Phenomena*" explains the role of proteins and emulsifiers in providing stability to colloidal dispersions, such as emulsions and foams, by modifying the interparticle colloidal forces as well as interfacial rheological properties. His research focuses on the role of proteins and other biomacromolecules on the structure, formation, stability and rheology of food emulsions, foams, and dispersions, with emphasis on (i) Adsorption of proteins at interfaces and (ii) Transport phenomena in dispersed systems. He teaches graduate level courses in *Colloidal Phenomena in Food & Biological Systems* and *Transport Phenomena in Food & Biological Engineering*, as well as undergraduate courses in *Food Process Engineering* and *Thermodynamics*.