Polymer and Colloidal Models Describing Structure-Function Relationships

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Annu. Rev. Food Sci. Technol. 2012. 3:405–24

The *Annual Review of Food Science and Technology* is online at food.annualreviews.org

This article's doi:
10.1146/annurev-food-022811-101250

1941-1413/12/0410-0405$20.00

Keywords

soft matter, mesoscopic scale, state diagram, fractal, scaling law, viscoelasticity

Abstract

Colloidal and polymer systems are not only abundant in food but also useful for gaining insights into structure-function relationships of food. Colloid and polymer systems are composed of mesoscopic scale particles dispersed in a liquid. Because of a relatively small potential barrier against aggregation between mesoscopic particles, a small change in temperature, pH, or chemical compositions can trigger aggregation and induce remarkable changes in structure and function of colloidal and polymer systems. An aggregated state is not normally an equilibrium state but a kinetically trapped state also called a jammed state. Various kinetic factors in food processing, such as the rate of changes in temperature, water content, and chemical compositions, must be taken into account to establish a complete state diagram of colloid- and polymer-based food systems.

INTRODUCTION

Food is regarded as one of the most complex types of soft matter (Mezzenga et al. 2005, Ubbink et al. 2008, van der Sman & van der Goot 2009). Soft matter is a generic term that has become popular in the past two decades for describing a large class of materials that are easily deformable and cannot be classified as gas, simple liquid, or hard solid (de Gennes 1991). A common feature of soft matter is that it consists of mesoscopic scale particles. The mesoscopic scale is an intermediate length scale between the microscopic and macroscopic scales and typically ranges from 1 nm to 1 μm. It is known that the shear modulus G of a material is proportional to λ^{-3} where λ is the length scale of the constituent particles (Likos 2001). Thus, G of a material constituted by mesoscopic particles (i.e., soft matter) is expected to be 3 to 12 orders of magnitude smaller than that of atomic compounds such as crystals.

Colloidal systems consist of mesoscopic particles dispersed in a continuous phase. Milk containing fat globules, casein micelles, and whey proteins dispersed in a continuous aqueous phase is an example of a naturally occurring colloidal system. The sizes of milk fat globules and casein micelles are typically of the order of 10 μm (Paquin 1999) and 100 nm (de Kruif 1998, Nishinari et al. 2000), respectively (**Figure 1**). The molecular weight of the major globular protein in milk, β-lactoglobulin, is 18,400 Da (Brownlow et al. 1997), approximately 10^3 times larger than that of water. The hydrodynamic radius of β-lactoglobulin is, however, only approximately 2 nm (Aymard et al. 1996a), approximately 10 times that of water, indicating an extremely compact tertiary structure of the globular protein.

Biopolymers are long chains of monomers or repeating units. Proteins and polysaccharides are abundant food biopolymers that play critical roles as structuring and functioning elements and also nutrients and energy reservoirs. The contour length of food biopolymers can be as long as a few μm (Ikeda et al. 2004a). Because of its size, the dynamics of polymer molecules are much slower than those of small molecules. For example, the dielectric relaxation time in an aqueous solution of small molecules, such as water (Petong et al. 2000) and monosaccharides (Fuchs & Kaatze 2001, Ikeda et al. 2011), is found to be of the order of 1–10 ps, whereas that of polysaccharides is approximately 0.1–1 μs (Ikeda et al. 1997a,b; Ikeda & Kumagai 1997, 1998). Slow dynamics of polymer molecules are reflected upon the time-dependent physical properties of polymer systems such as viscoelasticity (Doi & Edwards 1986). Polymers are thus widely used in the food industry as physicochemically functional ingredients for engineering the stability and texture of food products (Morris 1998, Walstra 2003).

The objective of this paper is to outline general principles and experimental findings in structure-function relationships in colloidal and polymer systems relevant to food. Viscoelastic properties are highlighted because of their significance as a determinant factor of the quality of food. In the subsequent section, colloidal systems are reviewed first in order to facilitate understanding of fundamental concepts of mesoscopic scale physics. Analogies and differences between

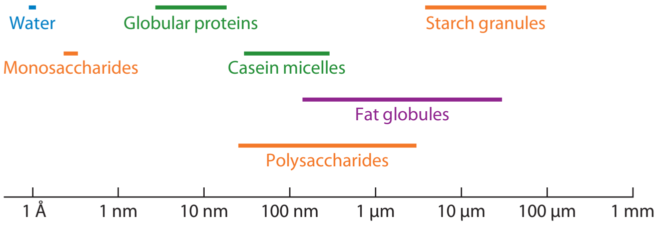

Figure 1

Length scales relevant to colloidal and polymer food systems.

colloidal and polymer systems are then depicted. Finally, perspectives toward engineering food structure and function are presented from the viewpoint of colloid and polymer sciences.

STRUCTURE-FUNCTION MODELS FOR COLLOIDAL SYSTEMS

In the following sections, colloidal systems are classified on the basis of the volume fraction of constituent particles and the nature of interaction between particles.

Colloidal Interactions

The van der Waals potential between two atoms V_a is given by the following equation:

$$V_a = -C\left(\frac{a_o}{r}\right)^6, \tag{1}$$

where C is a constant typically smaller than the magnitude of the thermal energy k_BT, k_B is the Boltzmann constant, T is the absolute temperature, a_o is the radius of the atom, and r is the distance between the atom centers. Equation 1 suggests that the van der Waals potential between two atoms separating at a distance of a_o is already weaker than the thermal energy.

The attractive interaction potential between two colloidal particles V_c can be calculated as the sum of van der Waals attraction between each atom in one of the particles and all the atoms in another particle. Assuming that the radius of the colloidal particles R_p is sufficiently larger than the separation distance between the particle surfaces h ($R_p \gg h$), the sum can be approximated by the following equation:

$$V_c \cong -A\frac{R_p}{h}, \tag{2}$$

where A ($= n^2Ca_o{}^6$) is the Hamaker constant, and n is the number density of atoms in the particle. As $n \cong a_o{}^{-3}$, the magnitude of the Hamaker constant A is of the same order as that of C. Therefore, van der Waals attraction between colloidal particles is larger than that between atoms by a factor of approximately R_p/h. When $R_p = 100$ nm and $h = 1$ nm, this factor becomes 100.

Colloidal particles dispersed in a liquid are in constant Brownian motion. The magnitude of the kinetic energy of a particle in Brownian motion is of the same order as that of the thermal energy. If two particles come into contact, they stick to each other and do not come apart because of the attractive potential being much greater than the kinetic energy. A common technique for preventing colloidal aggregation is to induce charges on particle surfaces (Weiss & McClements 2000). When the particle surface is charged, oppositely charged ions accumulate in the vicinity of the surface. The electrostatic potential ψ decays exponentially with increasing distance from the surface. The repulsive interaction potential between two colloidal particles V_e also decays exponentially with increasing separation distance between the particle surfaces h.

The classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory describes colloidal interactions as a balance between the van der Waals attraction and electrostatic repulsion (Hunter 1986, Likos 2001). **Figure 2*a*** shows examples of the total interaction potential between colloidal particles V_t.($= V_c + V_e$) as impacted by ionic strength. As two colloidal particles approach due to Brownian motion, the chance of their aggregation depends on the existence and magnitude of the potential barrier (V_b). When V_b is sufficiently greater than k_BT, Brownian motion is insufficient to overcome the barrier, and the two particles are repelled to keep separated. As the salt concentration increases, the magnitude of V_b decreases and aggregation becomes more likely. The DLVO theory suggests that some colloidal systems may not be in equilibrium even if they appear to be stable for hours or days.

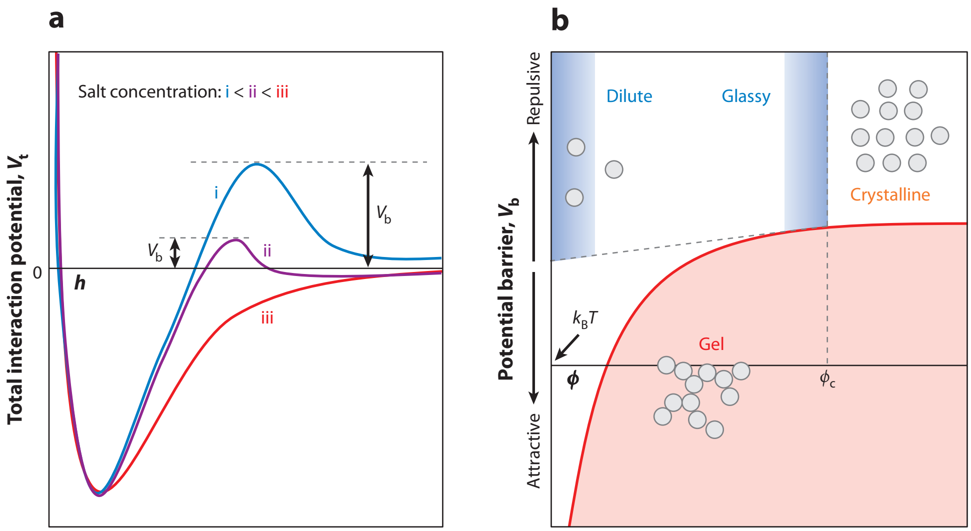

Figure 2

(*a*) Interaction potential between colloidal particles. V_b, potential barrier. (*b*) Schematic state diagram of colloidal systems. Abbreviations: *h*, separation distance between the particle surfaces; ϕ, volume fraction of particles; ϕ_c, close packing volume fraction of particles; k_B, Boltzmann constant; *T*, absolute temperature.

In practice, DLVO theory usually is not directly applied for food systems owing to several factors. Food colloidal particles are hardly perfect spheres because molecules or their segments on the particle surface have varying affinity to the solvent (Dickinson 2008; Ikeda et al. 2005; Nakamura et al. 2003, 2004) that may introduce repulsive steric hindrance against particle aggregation. Other physical forces due to hydrophobic interactions, hydrogen bonds, and biological affinity are common in food colloids. Further, because of complexity and heterogeneity of food systems, depletion flocculation may be a significant factor in stability of colloidal particles, and this is typically observed for a system with two groups of structures that have significantly different dimensions (Blijdenstein et al. 2004, Tuinier 2003). Quantitative descriptions of these interactions in combination with DLVO forces are beyond the scope of this paper.

Dilute Systems with Repulsive Interactions

The presence of a particle in a flowing liquid disturbs the flow, leading to an increased dissipation of kinetic energy. This results in an increased resistance to the flow. In other words, dispersed particles increase the effective viscosity of the entire system. Relationships between colloidal structure and viscosity in dilute conditions (**Figure 2*b***) are reviewed in this section.

Hard spheres. Colloidal interactions are negligible when the volume fraction of particles (ϕ) is sufficiently low (e.g., $\phi < 0.01$). The relative viscosity (η_r) of a dilute dispersion of spherical rigid particles can be described by the Einstein's equation of viscosity (Einstein 1911),

$$\eta_r = \frac{\eta_c}{\eta_m} = 1 + 2.5\phi, \tag{3}$$

where η_c is the viscosity of the colloidal dispersion, and η_m is the viscosity of the medium.

Nonspheres. When dispersed particles are rigid but not spherical, the relative viscosity of a dilute dispersion is given by the following equation (Simha 1940):

$$\eta_r = 1 + k(p)\phi, \tag{4}$$

where $k(p)$ is a dimensionless number called the Einstein-Simha constant, and p is the aspect ratio of the particle. The aspect ratio of spherical particles equals unity, and the constant equals 2.5 [i.e., $k(1) = 2.5$]. For nonspheres, $k(p)$ is known to be an increasing function of p (Yao & Matsumoto 1987). The viscosity of colloidal systems thus increases with increasing anisotropy of dispersed particles.

Soft spheres. Soft particles are compressible and/or deformable. The relative viscosity of a dilute dispersion of liquid or gas droplets is given by the following equation when the deformation of the droplets is sufficiently small (Taylor 1932):

$$\eta_r = 1 + \left(\frac{\eta_m + 2.5\eta_d}{\eta_m + \eta_d}\right)\phi, \tag{5}$$

where η_d is the viscosity of the dispersed phase (i.e., a liquid or gas). Equation 5 equals Einstein's equation of viscosity if $\eta_d \gg \eta_m$. At the other extreme, where $\eta_d \ll \eta_m$ (e.g., a viscous liquid containing air bubbles), Equation 5 leads to

$$\eta_r = 1 + \phi. \tag{6}$$

It is possible to extend Equation 5 to be applicable to the case that the deformation of droplets is not negligible (Schowalter et al. 1968), although the mathematical expression is quite complicated for practical uses.

Nondilute Systems With Repulsive Interactions

As the volume fraction of particles increases, hydrodynamic interactions between particles become more pronounced. To describe the viscosity in such a nondilute condition, Krieger & Dougherty (1959) incorporated the close packing volume fraction of particles (ϕ_c) into Einstein's equation (Hunter 1986):

$$\eta_r = \left[1 - \frac{\phi}{\phi_c}\right]^{-[\eta]\phi_c}, \tag{7}$$

$$[\eta] = \lim_{\phi \to 0} \frac{\eta_r - 1}{\phi}, \tag{8}$$

where $[\eta]$ is the intrinsic viscosity, which is a measure of a solute's contribution to the viscosity at infinite dilution. Equation 7 equals Equation 3 in the dilute limit of hard spheres ($\phi \to 0$) because the intrinsic viscosity equals 2.5.

For hard spheres, ϕ_c is approximately 0.634 (Song et al. 2008). The viscosity of an aqueous dispersion of hard spheres increases as the volume fraction of spheres approaches ϕ_c and diverges to infinity at ϕ_c (Meeker et al. 1997). As indicated in **Figure 2*b***, a glassy state may be observed near ϕ_c (van der Vorst et al. 1995, Dawson 2002). The glassy state is an amorphous or noncrystalline state of hard matter. Becuase of an extremely high viscosity, it is quite difficult to achieve the state of equilibrium of a glassy material in the laboratory. Within realistic timescales of observation, a glassy material may behave as a solid, exhibiting elasticity instead of viscosity (Lindsay & Chaikin 1982, Dahbi et al. 2010). Mayonnaise is an example of a system consisting of closely packed soft particles. Due to the deformability of closely packed oil droplets, mayonnaise is not so hard as a glass but does exhibit elasticity (Bengoechea et al. 2009, Su et al. 2010, Thakur et al. 2008).

Most mathematical models for describing rheological properties of colloidal systems are expressed as a function of the volume fraction of the colloidal particles. The impact of colloidal interactions on rheological properties can then be integrated into such models using an effective volume fraction ϕ_{eff} of colloidal particles (Mewis & Macosko 1994):

$$\phi_{\text{eff}} = \phi \left(1 + \frac{\delta}{R_{\text{p}}}\right)^3, \tag{9}$$

where δ is defined as one-half of the closest separation distance between two particles with an identical radius of R_{p}. In a colloidal system that can be described within the framework of the DLVO theory, δ is related to the Debye screening length ($1/\kappa$) as follows:

$$\delta = \kappa^{-1} \ln \left[\frac{\alpha}{\ln(\alpha/(\ln \alpha))}\right], \tag{10}$$

$$\alpha = 4\pi \varepsilon \psi R_{\text{p}}^2 \kappa \exp\left(\frac{2 R_{\text{p}} \kappa}{k_{\text{B}} T}\right), \tag{11}$$

where ε is the permittivity or the dielectric constant of the continuous phase, and ψ is the electrostatic potential. The Debye screening length corresponds to the characteristics distance over which the surface charges have significant influence. In an aqueous solution of NaCl, the screening length is calculated to be approximately 10 nm at a concentration of 1 mmol dm^{-3} and approximately 0.3 nm at 1 mol dm^{-3}.

In the presence of long-range repulsive interactions, such as electrostatic repulsions between particles, the effective volume fraction ϕ_{eff} may reach the close-packing volume fraction ϕ_{c} while particles are still separated. Then, particles can be aligned into a crystalline lattice, such as a body-centered-cubic or face-centered-cubic lattice (Lindsay & Chaikin 1982, Robbins et al. 1988, van der Vorst et al. 1995). These types of dispersions behave as elastic solids but can be distinguished from colloidal glasses that also exhibit elasticity based on the observation of Bragg scattering characteristics of crystalline structure (Lindsay & Chaikin 1982). Aqueous dispersions of various globular proteins, such as bovine serum albumin (Ikeda & Nishinari 2000, 2001b; Inoue & Matsumoto 1996), β-lactoglobulin (Ikeda et al. 2000, Ikeda & Nishinari 2001b), ovalbumin (Ikeda & Nishinari 2001a,b; Inoue & Matsumoto 1996; Matsumoto & Inoue 1993; Matsumoto et al. 1992), and rat serum albumin (Inoue & Matsumoto 1996), have been found to exhibit elasticity at relatively low protein concentrations (e.g., 0.1% by weight), although the origin and nature of long-range repulsive interactions between protein molecules are not fully understood.

Dilute Systems With Attractive Interactions

Aggregation between particles in Brownian motion (i.e., perikinetic aggregation) is known to result in the formation of fractal flocs. The formation of fractal flocs has been investigated for various food proteins, such as bovine serum albumin (Hagiwara et al. 1996, 1997a, 1998; Kumagai et al. 1999), casein (Bremer et al. 1989, 1993; Hagiwara et al. 1997b; Zhong et al. 2004b,c, 2007), β-lactoglobulin (Aymard et al. 1996b; Gimel et al. 1994; Hagiwara et al. 1997a,b), soybean globulin (Hagiwara et al. 1997b), and whey protein isolate (Ikeda et al. 1999, 2000; Ikeda & Foegeding 1999; Ikeda & Morris 2002; Vreeker et al. 1992).

Fractal concepts. Fractal is a geometric concept for describing self-similar structure that appears similar at any length scales of observation. It is impossible to find a characteristic length in self-similar structure, but it is still possible to characterize self-similar structure using a parameter

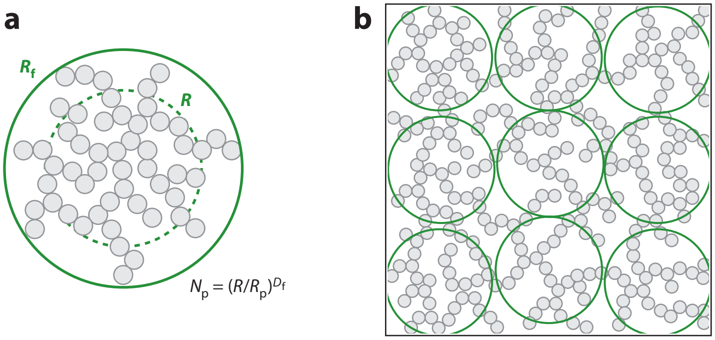

Figure 3

(*a*) Cross-section of a fractal floc. (*b*) Closely packed fractal flocs. Abbreviations: R, radius of an imaginary sphere placed within a fractal floc; R_f, the radius of the floc; N_p, number of particles in the imaginary sphere; R_p, radius of the particle; D_f, fractal dimension.

called fractal dimension D_f. As a square can be divided into 2^2, 3^2, 4^2, ... n^2 identical squares, a square can be said to have a dimension of two. Likewise, self-similar structure can be divided into 2^{Df}, 3^{Df}, 4^{Df}, ... n^{Df} identical structures. Now, consider an imaginary sphere with a radius of R placed within a fractal floc (**Figure 3*a***). The number of particles N_p in this imaginary sphere is expressed by the following equation:

$$N_p = \left(\frac{R}{R_p}\right)^{D_f}, \qquad (12)$$

where R_p is the radius of the particle. Equation 12 indicates that the number of particles in a spherical space with a certain radius increases with increasing D_f. In general, the structure in a fractal object becomes coarser or denser with decreasing or increasing fractal dimension, respectively.

The effective volume fraction of particles is considered to equal the volume fraction of flocs:

$$\phi_{\text{eff}} = \phi \frac{1}{N_f}\left(\frac{R_f}{R_p}\right)^3 = \phi\left(\frac{R_f}{R_p}\right)^{3-D_f}, \qquad (13)$$

$$N_f = \left(\frac{R_f}{R_p}\right)^{D_f}, \qquad (14)$$

where N_f is the number of particles in a floc. For fractal flocs formed by food proteins, D_f values of approximately two have been frequently reported (Clark 1998, Mehalebi et al. 2008). In such a case, the effective volume is approximately proportional to the R_f/R_p ratio, even though the total number of molecules in the system remains the same.

Nondilute Systems With Attractive Interactions

The viscosity in an aggregated system increases with increasing volume fraction of flocs and diverges when flocs are percolated or connected throughout the system. At higher volume fractions, elastic gels are formed (**Figure 2*b***).

Scaling laws. Scale invariance is an important feature of fractal objects. A scale-invariant physical law is also called a scaling law. These scaling laws are expressed as power-law functions [i.e., $f(x) = ax^k$, where a and k are constants, and x is a variable] because power-law functions are mathematically scale invariant in that a change in the scale of the function's argument (i.e., $x \rightarrow cx$, where c is a constant) preserves the shape of the function [i.e., $f(cx) \sim f(x)$]. The exponent in a power-law function (k) is called the scaling exponent. Equations 12 and 13 derived for fractal structures are indeed in the form of power laws.

The shear modulus G of a gel in the vicinity of the gelation threshold ϕ_g is predicted to follow the subsequent scaling law (de Gennes 1979):

$$G \sim (\phi - \phi_g)^t. \tag{15}$$

The scaling exponent t has been shown to be 1.6–2.2 for globular proteins such as β-lactoglobulin, ovalbumin, and bovine serum albumin, and considered to indicate the formation of homogeneous networks by isotropic force percolation (Sagis et al. 2004; van der Linden & Sagis 2001; Veerman et al. 2002, 2003a). Larger values (approximately four) of the exponent, an indicative of central force percolation, have also been found for bovine serum albumin (Sagis et al. 2004, Veerman et al. 2003b).

The shear modulus becomes progressively less dependent on the volume fraction as the volume fraction increases (Mehalebi et al. 2008). In order to derive scaling laws for describing the elastic modulus at sufficiently large volume fractions, the system is assumed to be closely packed with fractal flocs (**Figure 3*b***) (Bremer et al. 1989, 1993; Shih et al. 1990). Stress applied to a floc is carried by a geometrically fractal elastic backbone of the floc. In the case that links between flocs are sufficiently strong, the elastic modulus G of the entire system is then given by

$$G \sim \phi^{(3+x)/(3-D_\mathrm{f})}, \tag{16}$$

where x ($=1.1 \sim 1.4$) is the fractal dimension of the elastic backbone in a floc (Shih et al. 1990). In the case that links between flocs are weak, the following equation is obtained:

$$G \sim \phi^{1/(3-D_\mathrm{f})}. \tag{17}$$

It has been found that Equation 16 is applicable to hydrogels of bovine serum albumin and β-lactoglobulin containing added $CaCl_2$ (Hagiwara et al. 1997a) and casein gels (Zhong et al. 2004b,c, 2007), and that Equation 17 is applicable to hydrogels of bovine serum albumin, caseinate, β-lactoglobulin, and soy globulin prepared without the addition of salt (Hagiwara et al. 1997a, 1998).

STRUCTURE-FUNCTION MODELS FOR POLYMER SYSTEMS

Polymer molecules explained in this section are those composed of long chains of repeating units. Individual polymer molecules in an aqueous solution are constantly changing their conformations because of thermal motion. The degree of freedom of a polymer chain is much larger than that of a colloidal particle consisting of a single phase of gas, liquid, or solid. It is thus necessary to incorporate additional dimensions in the state diagram for describing the state of polymer systems.

Conformation of an Isolated Polymer Chain

In a simple treatment, a polymer chain is regarded as a linear chain of N segments of an identical length b (**Figure 4*a***), and segment-segment interactions are exclusively considered. In the case that any orientation is allowed between two adjacent segments, the chain is called ideal or Gaussian. The radius of gyration R_g of an ideal chain is given by the following equation:

$$R_\mathrm{g} = \frac{1}{\sqrt{6}} b N^{1/2}. \tag{18}$$

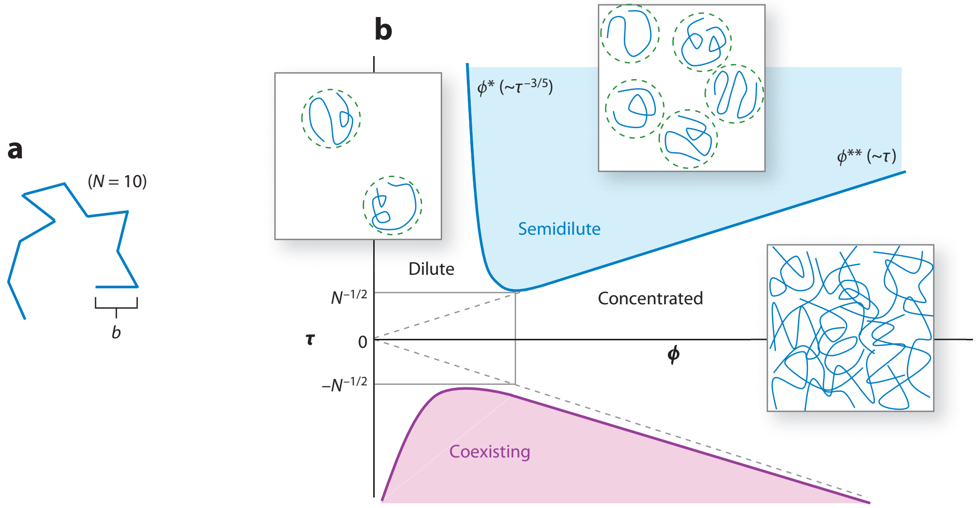

Figure 4

(*a*) Coarse-grained model of a polymer chain. The variable b represents the length of a polymer segment as described in the text. (*b*) Theoretical state diagram of polymer systems. Abbreviations: N, number of segments in a polymer chain; ϕ, volume fraction of the polymer; ϕ^*, boundary between dilute and semidilute regions; ϕ^{**}, boundary between semidilute and concentrated regions; τ, reduced temperature.

The contour length of this chain (bN) is approximately $N^{1/2}$ times larger than R_g, indicating that the polymer chain is coiled in a relatively compact shape.

In a real polymer chain, orientation between adjacent segments is restricted in a way that the chain cannot intersect itself. As a result, there exists a certain region around a segment where any other segments cannot exist. In this sense, interactions between polymer segments are essentially repulsive. The volume of this region is called the excluded volume. The radius of gyration of a real chain having an excluded volume is given by the following equation:

$$R_g \cong R_0 \left(\frac{N^{1/2} v}{b^3} \right)^{1/5} \sim b N^{3/5}, \tag{19}$$

where R_0 is the radius of gyration in the absence of the excluded volume effect (see Equation 18), and v is the so-called excluded volume parameter. By comparing Equations 18 and 19 with Equation 12, one may conceive that a polymer chain can be regarded as a fractal object. The fractal dimensions of an ideal chain and a real chain become 2 and 5/3, respectively. As a polymer chain is a fractal object, structure and function of polymer systems are frequently described using scaling laws.

The smaller value of the fractal dimension of a real chain indicates that a real chain is more expanded or swollen than an ideal chain. The intrinsic viscosity (Equation 8) is a measure of the volume of a polymer chain in a dilute solution and has been used to characterize the conformation of polymer chains (Chamberlain & Rao 2000; Cheng et al. 2002; Dou & Colby 2006; Goycoolea et al. 1995; Pamies et al. 2008, 2010; Rushing & Hester 2004; Sudduth 1997).

Many biopolymers are polyelectrolytes that are polymers having ionizable groups such as carboxyl, sulfuric acid, or amino groups (Morris 1998). When the ionic strength is sufficiently small, a polyelectrolyte chain is extended due to electrostatic repulsions between charged groups. As the ionic strength increases, electrostatic repulsions are more screened, and the chain conformation becomes more compact. Scaling laws for describing structure-function relationships of polyelectrolyte systems have been derived by considering the Debye screening length (Dobrynin et al. 1995).

Solvent Quality

For a polymer solution in reality, segment-segment interactions can be either repulsive or attractive, depending on segment-solvent interactions. Effects of the solvent on the excluded volume are considered in this section. The excluded volume parameter v is related to Flory's solvent-segment interaction parameter χ as follows:

$$v = v_c\left(\frac{1}{2} - \chi\right), \tag{20}$$

where v_c is a constant.

In a good solvent, in which $\chi < 1/2$, the excluded volume parameter is positive. A polymer chain is swollen. The radius of gyration of a polymer chain is expressed by Equation 19. The quality of this type of solvent is considered to be good.

In a poor solvent, in which $\chi > 1/2$, the excluded volume parameter becomes negative. Polymer segments dislike solvent molecules and tend to separate from the solvent. A polymer chain collapses into a compact globule that follows (Cordeiro 1999, Williams & Brochard 1981):

$$R_g \sim bN^{1/3}. \tag{21}$$

The quality of this type of solvent is considered to be poor.

In an ideal solvent, in which $\chi = 1/2$, the excluded volume effect is ineffective. A polymer chain is ideal and follows Equation 18. The quality of this type of solvent is ideal.

The temperature dependency of v is often expressed in the following form:

$$v = v_c(1 - \Theta/T), \tag{22}$$

where Θ is the theta temperature. Equation 22 indicates that the solvent quality can be manipulated by changing temperature without changing chemical compositions. At $T = \Theta$, v and χ equal zero and 1/2, respectively. For this reason, an ideal solvent is also called a theta solvent.

State Diagram

A theoretically derived state diagram of polymer systems is illustrated in **Figure 4*b***. The horizontal and vertical axes represent the volume fraction of the polymer and the reduced temperature τ, respectively (Cotton et al. 1976, Richards et al. 1981). The reduced temperature is related to the absolute temperature and the theta temperature as follows:

$$\tau = (T - \Theta)/\Theta. \tag{23}$$

The τ region between $\tau = N^{1/2}$ and $\tau = -N^{1/2}$ is called the theta region where polymer chains behave ideally, following Equation 18.

In the τ region above the theta region, the solvent quality is good. This good solvent region is divided by the following two lines:

$$\phi^* \sim \tau^{-\frac{3}{5}}, \tag{24}$$

$$\phi^{**} \sim \tau^1, \tag{25}$$

where ϕ^* represents the boundary between the dilute and semidilute regions, and ϕ^{**} represents the boundary between the semidilute and concentrated regions. The ϕ region below ϕ^* is the dilute region, where individual polymer chains are isolated. The radius of gyration of a polymer chain is expressed by Equation 19. At $\phi = \phi^*$, polymer chains begin to interpenetrate or overlap each other. As ϕ^* is estimated to be no larger than $N^{-4/5}$, polymer chains having $N = 10^5$ interpenetrate already at $\phi = 0.0001$. The ϕ region between ϕ^* and ϕ^{**} is called the semidilute region, where the concentration dependency of the viscosity is described by a scaling law with a predicted exponent value of 3.75 (de Gennes 1976b)

$$\eta \sim \phi^{3.75}. \tag{26}$$

At $\phi > \phi^{**}$, polymer chains are said to be concentrated. The system is so crowded that a segment of a polymer chain is surrounded by segments belonging to different chains rather than other parts of the self. In other words, excluded volume effects are shielded. Polymer chains in the concentrated region behave ideally, following Equation 18 (Candau et al. 1982, Daoud et al. 1975, Sun et al. 2007).

The solvent quality is poor in the τ region below the theta region, indicating that a polymer solution can be separated into a polymer-rich phase and a solvent-rich phase solely by lowering temperature without changing chemical compositions of the solvent. The poor solvent region is divided by a coexisting curve representing the compositions in the phase-separated polymer-rich and solvent-rich phases.

It should be noted that the glass transition is not included in **Figure 4*b***. Close packing of polymer chains in the coiled conformation does not induce a glass transition because polymer chains can interpenetrate or overlap. The formation of polymer glasses are observed at temperatures much lower than freezing temperatures (Hatakeyama & Hatakeyama 1998, Hatakeyama et al. 2004, Naoi et al. 2002) and in high solid systems (Coppola et al. 2008, Jiang et al. 2011, van der Sman & Meinders 2011) in which thermal motion of polymer chains is restricted.

Systems With Attractive Interactions

The concentration dependence of the viscosity in a semidilute solution of polysaccharide is described by a scaling equation. Experimentally determined values of the scaling exponent are approximately 3.3 for most polysaccharides, whereas larger values (i.e., 3.8–5.1) have been found for certain polysaccharies, such as galactomannans and xanthan gum (Doublier & Launay 1981, Launay et al. 1997, Morris et al. 1981, Robinson et al. 1982). The larger values of the scaling exponent are considered to be a signature of the presence of attractive interactions between polymer chains. Attractive interaction between polymer chains may induce the formation of mesoscopic structure.

Mesophase transition. Many types of food polysaccharides exhibit a conformational transition from a disordered coiled conformation to a double- or triple-stranded helical conformation upon a change in temperature and/or the solvent (Ikeda et al. 2001, 2004a,b; Ikeda & Nishinari 2001c; Ikeda & Shishido 2005; Morris 1998). A multiple-stranded helix is stabilized by a number of hydrogen bonds between strands and is much more rigid than an unassociated single polymer chain. Xanthan gum is a polysaccharide that forms particularly rigid helices and transforms from an isotropic phase (I) to first a biphasic phase (B) with increasing concentration and then to an anisotropic liquid crystalline phase (A), also called a mesophase (Maret et al. 1981, Lee & Brant 2002c). As illustrated in **Figure 5*a***, the biphasic phase is confined in a chimney-like narrow region at relatively high temperatures (Ginzburg et al. 1985, Shoji & Tanaka 2002). The viscosity increases with increasing concentration in the isotropic phase but decreases in the biphasic phase (Allain et al. 1988; Lee & Brant 2002a,b). Schizophyllan (Van & Teramoto 1982) and scleroglucan

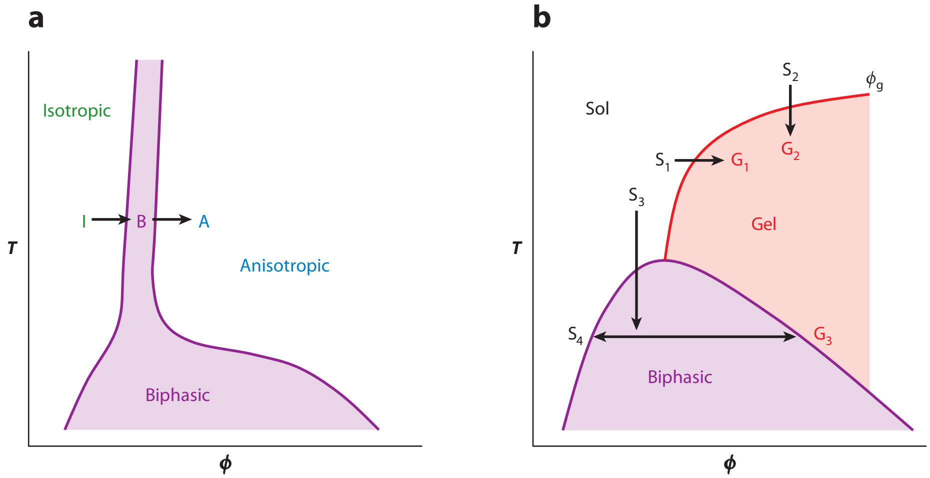

Figure 5

(*a*) Schematic state diagram of rod-like polymers. (*b*) Schematic state diagram of gelling polymers. Abbreviations: *T*, absolute temperature; ϕ, volume fraction of the polymer; I, a point in the isotropic phase; B, a point in the biphasic phase; A, a point in the anisotropic phase; S, a point in the sol phase; G, a point in the gel phase; ϕ_g, gelation threshold.

(Yanaki et al. 1984) are even more rigid polysaccharides and capable of forming mesophases. Aqueous solutions of these polysaccharides exhibit elasticity or a yield stress under certain conditions due to the formation of a three-dimensional network structure having a long relaxation time (Fang & Nishinari 2004, Fang et al. 2004, Grassi et al. 1996).

Sol-gel transition. Certain types of multiple-stranded helices of polysaccharides can aggregate to form a network structure. If the network is connected throughout the system, the network is said to be percolated and the system transforms from a liquid state to a gel state (**Figure 5*b***) (de Gennes 1979, Tanaka 2000a). A number of scaling laws have been derived for describing sol-gel transitions of polymer systems (de Gennes 1979, Martin & Adolf 1991), and their validities have been tested experimentally (Fujii et al. 2000, Richter 2007, Tari & Pekan 2009). The shear modulus of a gel in the vicinity of the gelation threshold is predicted to follow Equation 15 (de Gennes 1979). Experimentally determined values of the scaling exponent *t* have been reported to be 1.93 for agarose (Tokita & Hikichi 1987), 1.9 (Joly-Duhamel et al. 2002) and 2.05 (Kumagai et al. 1993) for gelatin, and 2.07 for polyacrylamide (Yano et al. 1993). Such exponent values are consistent with a prediction from a lattice percolation model assuming scalar forces between bonds (de Gennes 1979).

The shear modulus of a polymer gel becomes progressively less dependent on the volume fraction as the volume fraction increases (Clark & Ross-Murphy 1985, Gordon & Ross-Murphy 1975, Joly-Duhamel et al. 2002). In the high-limiting concentration range, it has been reported frequently that the shear modulus is proportional to the squared polymer concentration (Eldridge & Ferry 1949, te Nijenhuis 1981, Ross-Murphy 2007). For describing gels at sufficiently high concentrations, the following scaling law has been derived (Candau et al. 1982, de Gennes 1976a):

$$G \sim \phi^{2.25}. \tag{27}$$

An experimentally determined value of 2.24 has been reported for curdlan (Lo et al. 2003).

In the derivation of Equation 27, the gel network is assumed to be composed of flexible strands. However, atomic force microscopy images of hydrogels and networks of biopolymers have revealed that the network is composed of seemingly rigid fibrous strands formed by lateral association of helices (Gunning et al. 1996, Ikeda et al. 2004b, Mackie et al. 1998). Joly-Duhamel et al. (2002) have derived scaling exponents of 1.5 for absolutely rigid strands linked loosely, 2.5 for semiflexible strands linked loosely, and 2.0 for semiflexible strands linked rigidly, and confirmed that the first exponent is applicable to gelatin gels.

In **Figure 5*b***, typical pathways of sol-to-gel transitions are indicated as $S_1 \rightarrow G_1$ (an increase in concentration) and $S_2 \rightarrow G_2$ (cooling). An alternative pathway starting from a solution (S_3), the volume fraction of which is below ϕ_g, is also shown in the figure. The solution (S_3) is driven into the biphasic region by lowering the temperature to induce phase separation. Gelation occurs if the polymer-rich phase (G_3) forms the continuous phase (Bulone et al. 2004, Matsuo et al. 2002, San Biagio et al. 1996, Xiong et al. 2005). Structure and function of this type of gels are influenced by various thermodynamic factors, such as the rate and the depth of quenching. It was initially considered that spinodal decomposition from relatively deep quenching is required for the polymer-rich phase to become the continuous phase (Bulone et al. 2004, Matsuo et al. 2002, San Biagio et al. 1996), and it was later shown that gelation can occur through a nucleation and growth mechanism (Xiong et al. 2005). Furthermore, a novel mechanism of phase separation has been found in polymer and colloid systems, and designated as viscoelastic phase separation (Tanaka 2000b, 2009; Tanaka & Nishikawa 2005), in which viscoelastic force balances between separating phases act as the driving force for the formation of transient network or cellular structures by the minority phases, such as the polymer- or colloid-rich phase.

ENGINEERING STRUCTURE AND FUNCTION OF COLLOIDAL AND POLYMER FOODS

Most foods are dispersed systems containing structural heterogeneity (Walstra 2003). It is generally impossible to predict and control macroscopic properties of a dispersed system based solely on the full description of chemical compositions without knowledge of the spatial distribution of chemical compounds or the structure. This means that qualities of food products having exactly identical chemical compositions can still vary, depending on the level of heterogeneity in internal structure.

Because many food systems can be described by colloidal and/or polymer models, the models interpreting structure-function relationships serve as foundations to engineering food functionality. In a broad sense, these relationships can be used to guide food processing that typically involves the following three steps: (*a*) the destabilization and destruction of the existing structure; (*b*) the creation of a new structure; and (*c*) the stabilization of the newly created structure (van der Sman & van der Goot 2009). The destabilization can be achieved in various ways, including changes in pH, temperature, and solvent compositions (de Kruif 1998, de Kruif et al. 1995). The creation of a new structure can occur spontaneously, driven by thermodynamic forces toward equilibrium, and complete at equilibrium. In other cases, structural transformation is driven by external forces and halted by jamming, a synonym for kinetic trapping of a structure or arresting of dynamics. Jamming occurs if an external stress is applied to a concentrated system (Cates et al. 1998) or the attractive interaction potential between particles is sufficiently large (Liu & Nagel 1998, Trappe et al. 2001). Aggregates, gels, and glasses are typical examples of jammed states (Dawson 2002, Trappe et al. 2001, Trappe & Sandkuhler 2004). Structure and function of jammed systems are influenced by a number of kinetic factors, such as the rate of changes in temperature and compositions (Matsuo et al. 2002; San Biagio et al. 1996; Xiong et al. 2005; Zhong & Daubert 2004;

Zhong et al., 2004a,b,c). Construction of thorough state diagrams that include the description of jammed states are urgent needs for identifying the optimum processing route for engineering a desired food structure and function (Cuq et al. 2003, van der Sman & van der Goot 2009).

CONCLUDING REMARKS

Colloid and polymer sciences that have advanced as individual branches of science are being systematically understood within the framework of soft matter physics. Both systems are constituted by mesoscopic particles, the size of which typically ranges from 1 nm to 1 μm. These systems are frequently found to be in a nonequilibrium state called a kinetically arrested state or jammed state because the attractive interaction potential between mesoscopic particles is generally greater than the magnitude of the thermal energy. A state diagram that includes a jammed state serves as a useful tool for predicting and controlling structure and function of these systems. Colloidal and polymer systems not only represent certain classes of food structures by themselves but also provide scientific insights into structure-function relationships of food. Food is an extremely complex dispersed system, the physicochemical functions of which cannot be predicted solely from its chemical compositions. Further advancement in soft matter physics is expected to enable us to quantitatively predict the state of food and provide a foundation for engineering food structure and function.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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