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Elasticity of high-volume-fraction fractal aggregate networks: A thermodynamic approach

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The elastic modulus of a colloidal aggregate network is dependent on the amount and spatial distribution of mass, as well as particle properties including size, shape, and particle-particle interactions. At high volume fractions, the elastic properties of a network of close-packed particle flocs is dependent on the strength of the interfloc links. A previously developed weak-link fractal scaling theory relates the elastic constant (K) of the network to the volume fraction of solids (Φ), namely $K \sim \Phi^{1/(3-D)}$. In this paper, we extend this theory to include a pre-exponential factor and obtain an exact expression for relationship between the Young's modulus and the volume fraction of solids.

INTRODUCTION

The structural network of many soft viscoelastic materials of industrial interest is the product of an aggregation process of molecules into particles, and of particles into increasingly larger clusters, until a space-filling three-dimensional network is formed (Fig. 1). Macroscopic properties such as hardness, opacity, and structural stability are directly influenced by this underlying network. Of particular importance is the relationship between network structure and elastic properties. Mathematical formulations for the relationship of the elastic modulus of an aggregate network to the amount and spatial distribution of network mass have been developed using fractal scaling relationships.[1–10] However, the elastic modulus is not solely influenced by the amount and spatial distribution of network mass, but also by particle properties, including size, shape, rigidity, and particle-particle interactions.[5,7–9] A general formulation for the relationship between the elastic modulus and the amount of solid material in an aggregate network, considering both particle properties and their spatial distribution in the network, is therefore required.

Early developments of a theory to explain the elastic properties of colloidal gels were carried out by Brown and Ball at Cambridge.[1] Brown and Ball proposed a power-law dependence of the shear elastic modulus of a colloidal aggregate network on the volume fraction of network mass, where the exponent of the volume fraction term was related to the mechanism of particle aggregation. This formulation was subsequently verified experimentally, and the theory further developed by other groups.[3–5,7] In 1990, Shih *et al.*[6] outlined the development of a scaling theory to explain the elastic properties of colloidal gels by again considering the structure of the gel network, like their predecessors did, as a collection of close-packed fractal flocs of colloidal particles (Fig. 1). However, these authors also defined two separate rheological regimes depending on the relative strength of the interfloc links *vis-a-vis* that of the flocs. Their formulation of the strong-link regime (applicable at low volume fractions), where the flocs yield under an applied stress, was identical to that of Brown and Ball. Their formulation of the weak-link regime (applicable at high volume fractions), where the interfloc links yield under an applied stress, differed from that suggested by Brown and Ball. The main objective of the above-mentioned studies was to explore the influence of the spatial distribution of network mass on elastic properties, and to infer a particle aggregation mechanism responsible for network formation. However, the elastic properties of such materials are not solely influenced by the amount and spatial distribution of network mass, but also by particle properties, including size, shape, rigidity, and particle-particle interactions.[5,7–9] A general formulation for the relationship between the elastic modulus and the amount of solid material in the gel network, considering both particle properties and their spatial distribution in the network is therefore required. In this paper we develop such a model, maintaining consistency with the model developed by Shih *et al.*[6]

MODEL

According to thermodynamic theory, the change in free energy (∂G) of a system at constant pressure, volume, and temperature equals the change in internal energy (∂U) minus the product of the change in entropy (∂S) times temperature (T):

$$\partial G = \partial U - T\partial S. \tag{1}$$

The change in free energy of a flocculated colloidal network as a function of changes in strain ($\partial\gamma$), at constant temperature, pressure (P), volume (V), and composition (μ), where deformation takes place without any rupture of bonds, has been shown by Sonntag, Strenge, and Schilov[11] to equal the product of stress (σ) times volume:

$$\left(\frac{\partial G}{\partial\gamma}\right)_{T,P,V,\mu} = \left(\frac{\partial U}{\partial\gamma}\right)_{T,P,V,\mu} - T\left(\frac{\partial S}{\partial\gamma}\right)_{T,P,V,\mu} = \sigma\cdot V. \tag{2}$$

The main assumption in this model is that the change in free energy of the network upon deformation arises due to changes in elastic energy (∂E), namely,

$$\frac{\partial G}{\partial\gamma} = \frac{\partial E}{\partial\gamma}. \tag{3}$$

The elastic energy of the network can be expressed in terms of deformation (ΔL), or strain ($\gamma = \Delta L/L$):

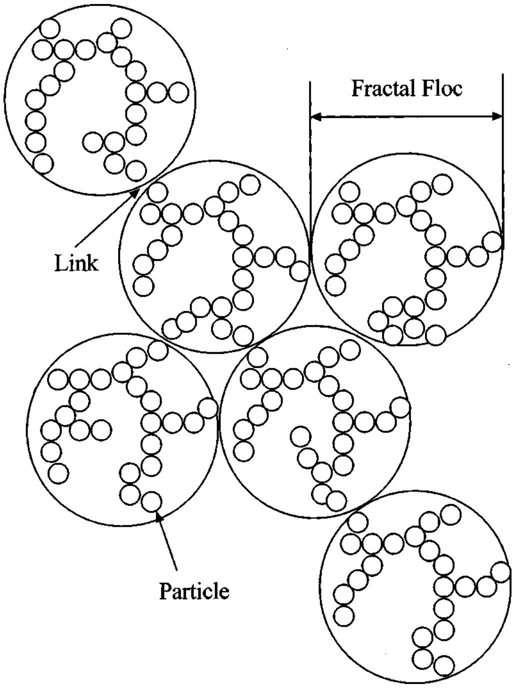

FIG. 1. Putative microstructure of a fractal colloidal aggregate network.

$$E=\frac{1}{2}k(\Delta L)^2=\frac{1}{2}L^2k\gamma^2, \tag{4}$$

where k is the elastic constant of the network. The elastic constant k can be substituted by $A\varepsilon/L$, where ε corresponds to the Young's modulus, A is the area over which the force is acting, and L is the size of the system. The product of the area times the length corresponds to the volume of the network, while the product of the Young's modulus times the strain corresponds to stress (σ). Thus, the change in elastic energy as a function of strain can be expressed as

$$\frac{\partial E}{\partial\gamma}=\frac{\partial}{\partial\gamma}\left(\frac{1}{2}LA\varepsilon\gamma^2\right)=V\varepsilon\gamma=V\sigma. \tag{5}$$

Sonntag and Strenge[12] have shown that the entropic contribution to the change in free energy of a flocculated colloidal network upon a small elastic deformation is much smaller than the contribution from changes in the internal energy of that network. Thus, for the case where $\partial U \gg T\,\partial S$,

$$\frac{\partial G}{\partial\gamma}\approx\frac{\partial U}{\partial\gamma}=V\varepsilon\gamma. \tag{6}$$

Upon integration and rearrangement, an expression for the Young's modulus of the network can be obtained:

$$\varepsilon=\frac{2\Delta U}{V\gamma^2}, \tag{7}$$

where ΔU corresponds to the change in the internal energy of the network upon deformation, which equals the total floc-floc interaction energy.

The volume of the system can be expressed as a function of the particle volume fraction (Φ) and the total volume occupied by the particles,

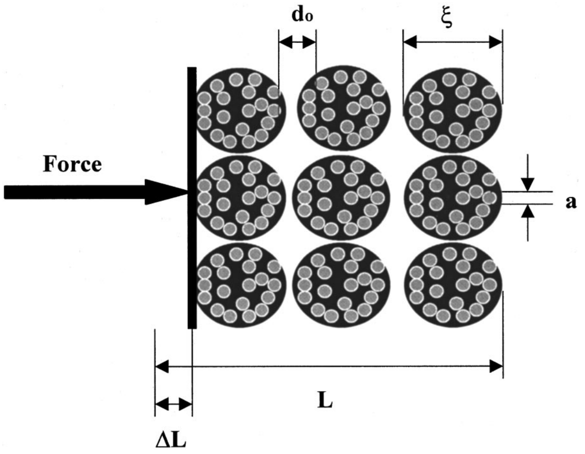

FIG. 2. Idealized flocculated colloidal network under compression. Particles (a) are packed in a fractal fashion within flocs (ξ). A force acting upon the network causes the links between flocs to yield, and the original length of the system in the direction of the applied force (L) to decrease (ΔL). Thus, the interfloc separation distance in the absence of an applied force (d_0) decreases.

$$V=\frac{V_aN_aN_\xi}{\Phi}, \tag{8}$$

where V_a is the volume of an individual particle, N_a is the number of particles in a floc, and N_ξ is the total number of flocs in the system. The number of particles in a floc is given by

$$N_a\sim\left(\frac{\xi}{a}\right)^D, \tag{9}$$

where ξ is the diameter of the flocs, a is the diameter of the particles within the floc, and D is the fractal dimension for the arrangement of particles within the floc. The volume fraction of particles within the floc (Φ_ξ) is therefore given by

$$\Phi_\xi\sim\frac{N_aV_a}{N_sV_s}\sim\left(\frac{\xi}{a}\right)^{D-d}, \tag{10}$$

where N_s is the number of available embedding space elements within the floc $[N_s\sim(\xi/a)^d]$,V_s is the volume of an element of embedding space, and d is the Euclidean dimension. At this point we will assume that a particle volume is equal to the volume of an element of embedding space, namely $V_a=V_s$. Thus, the diameter of the flocs varies with the volume fraction of particles within the floc as

$$\xi\sim a\Phi_\xi^{1/(D-d)}. \tag{11}$$

Flocs pack in a regular, close-packed, Euclidean fashion; hence, at the floc level of structure, the material can be considered as an orthodox amorphous substance. Within the flocs, however, particles pack in a non-Euclidean, fractal fashion. For such a structural arrangement, the volume fraction of particles in a floc (Φ_ξ) is equivalent to the volume fraction of particles in the entire system (Φ), namely $\Phi_\xi=\Phi$. This well-known relation of polymer physics[13] has been experimentally shown to also apply to colloidal aggregates above their gelation threshold.[14]

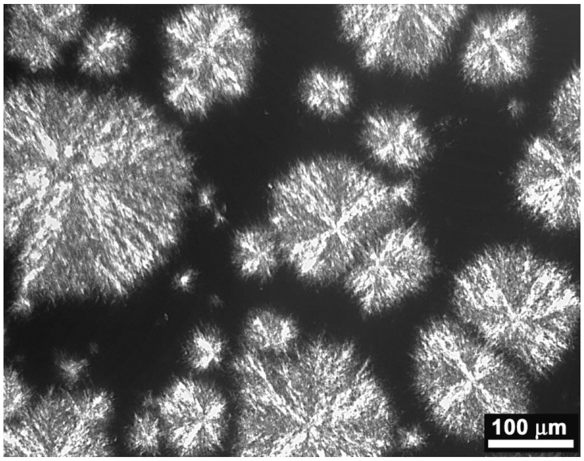

FIG. 3. Polarized light micrograph of the fat crystal network in milkfat crystallized at 22 °C demonstrating the existence of particles and particle flocs.

Thus, considering all of the above, for spherical particles packed in a fractal fashion within a floc, the Young's modulus of the network can be expressed as

$$\varepsilon \sim \frac{12\Delta U}{\pi a^3 N_\xi \gamma^2}\Phi^{d/(d-D)}. \qquad (12)$$

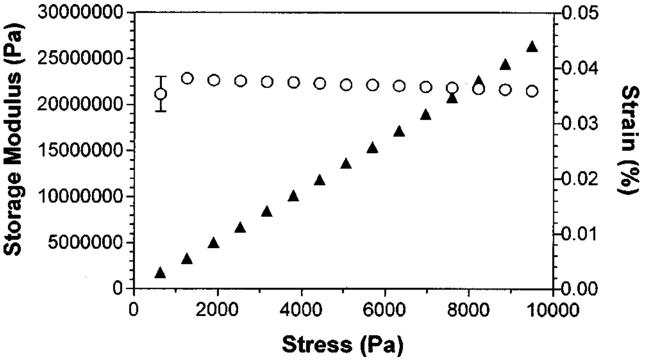

FIG. 4. Shear stress sweep of a tallow sample (5 °C, 1 Hz) demonstrating the existence of a linear elastic region of constant storage modulus (G') at very small strains.

In the weak-link rheological regime described by Shih *et al.*,[6] the links between flocs of colloidal particles yield under an external stress, i.e., the flocs are mechanically stronger than the links between them. Thus, in this regime, the macroscopic deformation of the network (ΔL) can be related to the interfloc deformation, $\Delta L = n(d_0 - d)$, where d_0 is the equilibrium distance between flocs, d corresponds to the distance between flocs under an applied stress, and n corresponds to the number of flocs in the direction of the applied stress (Fig. 2). The number of flocs in the direction of the applied stress roughly equals the number of links between flocs for the case where $L \gg \xi$. Substitution of one of the strain terms with $n(d_0 - d)/L$, L/n with ξ, ξ with $a\Phi^{-1/(d-D)}$, a^2 with $\xi^2\Phi^{2/(d-D)}$, and rearrangement, leads to the expression:

$$\varepsilon \sim \frac{12\left(\dfrac{\Delta U_\xi}{(d_0-d)}\right)}{\pi a \xi \gamma}\Phi^{1/(d-D)}, \qquad (13)$$

where $\Delta U_\xi (\Delta U_\xi = \Delta U/N_\xi)$ corresponds to the change in internal energy per floc-floc bond. Knowledge of the nature of interparticle interactions would allow for substitution of $\Delta U_\xi/(d_0 - d)$ for the expression of a force into Eq. (13).

For example, if the main type of interaction forces between the structural elements of a network are van der Waals' forces, substitution of $\Delta U_\xi/(d_0 - d)$ with the expression of a van der Waals' force allows for the calculation of the Young's modulus. The exact expression can vary dramatically depending on the morphology of the floc. For example, the interaction force between two spheres is $A\xi/12d_0^2$, two blocks $A\xi^2/6\pi d_0^3$, and between two objects with a shape intermediate between blocks and spheres, $A\xi^{1.5}/8d_0^{2.5}$.[15] Thus, expressions for the Young's modulus of a flocculated colloidal network, where the sole interaction forces are van

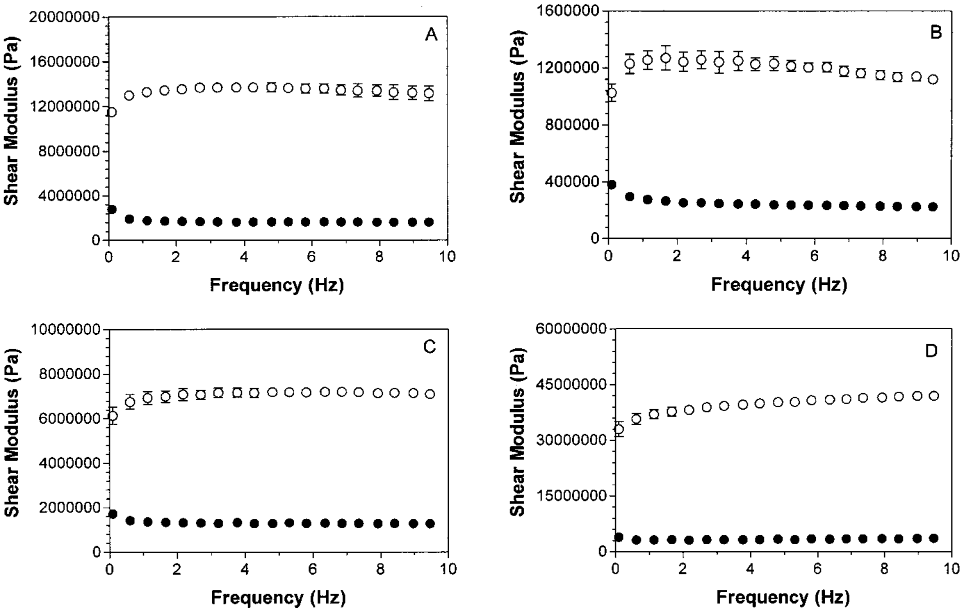

FIG. 5. Frequency sweeps of (A) palm oil at 5 °C, (B) lard at 5 °C, (C) milkfat at 5 °C, (D) cocoa butter at 20 °C. Dynamic stresses varied, depending on the sample, from 400 to 10 000 Pa. At these low stresses/strains, these plastic materials behave essentially as solids, indicated by the frequency independence of the storage modulus (G'), and the fivefold difference between storage (○) moduli and loss (●) moduli (G'').

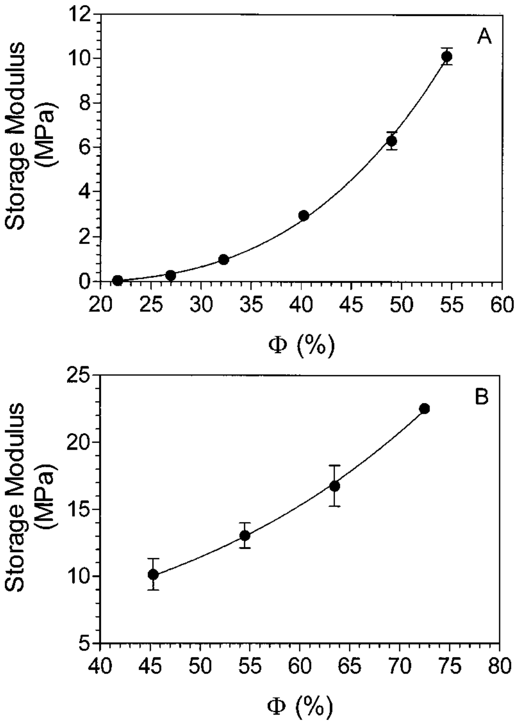

FIG. 6. Power-law dependence of the storage modulus (G') on the volume fraction of solids (Φ) for (A) palm oil and (B) tallow.

der Waals' forces, can be obtained for the case where the flocs are spheres (ε_S), blocks (ε_B), or a shape intermediate between that of spheres and blocks (ε_{SB}), namely,

$$\varepsilon_S \sim \frac{A}{\pi a \gamma d_0^2} \Phi^{1/(d-D)}, \tag{14}$$

$$\varepsilon_B \sim \frac{A\xi}{\frac{1}{2}\pi^2 a \gamma d_0^3} \Phi^{1/(d-D)}, \tag{15}$$

$$\varepsilon_{SB} \sim \frac{A\xi^{0.5}}{\frac{2}{3}\pi a \gamma d_0^{2.5}} \Phi^{1/(d-D)}, \tag{16}$$

where A is the effective Hamacker's constant (J) for the interaction between two flocs. The choice of model will depend on the morphological characteristics of the flocs within a particular network.

Our group has shown that crystal networks of triacylglycerols in fats are structured in a similar fashion as flocculated colloidal networks.[8] Upon crystallization, primary crystallites aggregate via mass and heat transfer-limited processes to form larger fractal clusters or flocs (Fig. 3), until a space-filling, continuous three-dimensional network is formed. The solidlike properties of such plastic materials are largely due to this underlying network of crystal aggregates. At low dynamic stresses/strains, these materials behave predominantly as solids, displaying a clear linear elastic region (Fig. 4). Storage moduli (G') in this region are independent of frequency, and are about fivefold higher than loss moduli (Fig. 5). Thus, at low stresses/strains, it is possible to characterize the elastic properties of these plastic soft materials, and to relate them to their structural features.

TABLE I. Comparison of theoretical and experimentally determined elastic moduli considering the morphology of the flocs.

System[a]	Φ (%)	D	ε_S (MPa)	ε_B (MPa)	ε_{SB} (MPa)	G' (MPa)
Tallow	72.5	2.41	6.59	8.39×10^4	14.0	22.5
Cocoa butter	75.2	2.37	9.10	1.16×10^5	1.93×10^3	60.0
Milkfat	53.3	2.59	5.72	7.28×10^4	1.21×10^3	6.90
Palm Oil	64.7	2.82	2.36	3.01×10^4	501	10.1
Lard	38.6	2.88	9.5×10^{-3}	121	2.01	1.25

[a] For all systems, $A = 5\times10^{20}$ J, $d_0 = 5$ nm, $a = 1\times10^{-6}$ m, $\xi = 100\times10^{-6}$ m (ε_B and ε_{SB}).

We also developed a structural and mechanical model which explained both the power-law dependence of the Young's modulus of such networks to solids' volume fraction (Fig. 6), and the influence of network structural features on the relative magnitude of the elastic modulus.[9] One of the problems with our model, though, was the inability to estimate several of the parameters in the pre-exponential term, and the fact that the derived relationships were not exact, but proportional. This made a direct calculation of the elastic modulus not possible. The model developed in this paper allows for the direct calculation of a Young's modulus for any high volume fraction aggregated particulate network from knowledge of the nature of interfloc interactions, and network structural characteristics. Our group has characterized the structural features of several fat crystal networks, and thus a value for the Young's modulus could be calculated and compared to experimental values (Table I). Interparticle and interfloc interactions in fat crystal networks take place solely via van der Waals' forces.[15,16] For certain systems, the agreement was quite good. Particularly encouraging was the fact that upon deformation, the combined interfloc separation distances could roughly account for the experimentally observed strain levels (about 0.01%), providing further support to weak-link rheological behavior in these high-volume fraction particulate aggregate networks. This is particularly important since in previous research, intercrystallite values in the range 0.4 to 2.0 nm (Refs. 15, 16) had been proposed. These values, however, are not realistic considering the strain levels imposed in dynamic rheological tests.[16]

An important conclusion from this work is that the shape of the clusters can greatly influence the value of the Young's modulus (Table I). It is not adequate, thus, to consider the shape of these clusters as spherical—knowledge of the morphology of the flocs is essential. Expressions for large body interactions considering particle morphology are sorely lacking in the literature. It would be advantageous if theory could be advanced in this area.

In conclusion, a general model for the relationship between the Young's modulus and the microstructure of high volume fraction aggregate networks has been obtained. The elastic properties of such materials are a function of the total amount of solid material present, the properties of the particles which make up the solid, and the spatial distribution of solid particles within the network. This model can be utilized to better understand and modify the macroscopic rheological properties of soft materials at high volume fractions.

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