Formation of Wide Range Ordered Arrangement in Microsphere Systems

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ABSTRACT: The origin of very wide range ordered arrangement composed of microspheres (or microgels) with narrow size distribution observed in solid state was investigated. To explain the mechanism of the formation, computer simulations by molecular dynamic method were adopted. When regularly arranged structure existed in random phase, ordered arrangement was grow up rapidly on the surfaces of the ordered structure. Newly created structure was the same to the former.

KEY WORDS Microgel / Microsphere / Arrangement Interface / Computer Simulation / Molecular Dynamics Interparticle Contact Angle /

Microsphere (microgel), or spherical polymer particle with diameter several tens of nm to several μm , and with narrow size distribution form ordered arrangement in liquid state,^{1–3} or also in solid state.^{4–6} Especially in solid state, ordered phase spreads to very large area (under appropriate conditions, it reaches 90%³), and only very few defects can be detected in solid state.³ The origin of this ordering is unclear. The mechanism of this ordering during cast has been explained as following. First microspheres form clusters with ordered structure in solution. Then as the solvent is removed, the clusters are gathered with their structure maintained. However the lack of the defects is not explained satisfactorily.

In this study, to make clear the origin of wide range ordered structure, computer simulation was carried out. For the simulation, effect of interface between ordered phase and random phase is considered.

SIMULATION

Simulation was carried out by molecular dynamics method with EPSON PC-386S per-

sonal computer. The method of simulation is essentially the same one that applied in liquid state. We have supposed that the structure of the arrangement is maintained through the drying because the motion of particles is greatly restricted in the concentrated state or in solid state.

Initially, particles are located randomly, then left moving under the influence of interparticle interactions calculated with D.L.V.O. theory.^{7,8} D.L.V.O. theory is composed of repulsive and attractive potentials. Potential energy of repulsion comes from electronic double layer and given by eq 1 for two particles with radii a .

$$V_R = 2\pi\epsilon a\psi^2 \ln[1 + \exp\{-\kappa(r-2a)\}] \quad (1)$$

where ψ is surface potential, r is distance between particle centers, κ is inverse double layer thickness, and γ is the permittivity of the dispersion medium. Potential energy of attraction V_A is essentially van der Waals energy, and given by

$$V_A = -\frac{Ha}{6} \left\{ \frac{2}{s^2-4} + \frac{2}{s^2} + \ln\left(1 - \frac{4}{s^2}\right) \right\} \quad (2)$$

where Ha is Hamaker constant and s is r/a .

In this study the following values are adopted. $\psi = 30 \text{ mV}$, $\kappa a = 2$, $\epsilon = 87.1 \times 10^{-10} \text{ C}^2 \text{N}^{-1} \text{m}$, $Ha = 1 \times 10^{-19} \text{ J}$. Interaction is calculated for each pair of particles with this potential, and the net force that contribute to the motion of a particle is approximated by sum of interaction. Then all particles are moved at once (1 time step).

At some instance, it is supposed that there appears ordered phase, and particles are affected by surface of ordered phase. Assuming these situations, ordered phase was fixed in the cell. The structure of fixed interface was assumed as 100 plane of face-centered cubic (FCC) structure which is usually observed in actual cases (Figure 1).

To determine the structure, interparticle contact angle (ICA)⁶ was calculated from the coordinate data of particles. When particles form ordered structure, contact angle of three particles is expected to become particular value. For example, in FCC structure interparticle contact angle is 60° , 90° , 120° , or 180° . And as increase the degree of arrangement, peaks in ICA distribution become sharp.

Figure 1. Schematic representation of cell for simulation.

So degree of arrangement can be evaluated quantitatively by standard deviation of ICA around particular angle.

RESULTS AND DISCUSSION

Effect of Interface with Ordered Structure

When interface existed in the cell, particles formed ordered arrangement rapidly, and very sharp peaks appeared at angle 60° , 90° , 120° , and 180° in ICA distribution (Figure 2). The sequence of planes are shown in Figure 3. This result reveals that formed structure is FCC, which is same to that of interface. Furthermore the sequence of planes are identical all over the cell, so it is considered that at the instance when small regularly arranged structure appears, ordered phase with no defects grew rapidly including interface in the cell.

Standard deviation of the contact angle formed by three spheres calculated for $90 \pm 10^\circ$ decreased with the arrangement. Under the existence of the ordered cluster, formation of arrangement occurs more rapidly than in completely random phase (Figure 4). In addition, the arrangement seemed to form at the nearest part of the interface first, and then extended to outer region (Figure 5). To confirm this supposition, the cell was divided by distance with the intervals corresponding to the distance between two particles in the ordered phase from the interface. And standard deviation of ICA was calculated for each region. Standard deviations decreased near the

Figure 2. Final distribution of interparticle contact angle determined under the influence of ordered interface.

Figure 3. Sequence of ordered planes newly formed in the cell under the influence of ordered interface.

Figure 4. The change of standard deviation of interparticle contact angle with time.

interface first, and then decreased at farther region (Figure 6). It is clear in Figure 6, that ordered structure was formed first at the nearest neighbour of the interface (around the ordered cluster), and then extended to outer region gradually.

Effect of Particle Density in Random Phase

In actual system, number density of particles in random phase is supposed to differ from that of interface. Considering this condition,

Figure 5. The change of positions of particles with time under the influence of ordered interface.

Figure 6. The variation of standard deviation of interparticle contact angle with time as a function of the distance between interface and particles. Distance from interface: ●, 0—0.5; ○, 0.5—1.0; □, 1.0—1.5, △, 1.5—2.0.

Figure 7. The variation of standard deviation of interparticle contact angle with time as a function of the distance between interface and particles. Distance from interface: ●, 0—0.5; ○, 0.5—1.0; □, 1.0—1.5; △, 1.5—2.0 ratio of particle density between random phase and interface = 90%.

Figure 8. The variation of standard deviation of interparticle contact angle with time as a function of the distance between interface and particles. Distance from interface: ●, 0—0.5; ○, 0.5—1.0; □, 1.0—1.5; △, 1.5—2.0 ratio of particle density between random phase and interface = 80%.

number density of particles was set at 90%, 80%, and 70% of the ordered cluster (interface). When density of particles was 90%, formed structure was same to that of the interface, and standard deviation of ICA decreased in the same way as in the previous case (decreased near the interface first, and then decreased at farther region (Figure 7)). When density of particles was 80%, particles near the interface formed the same structure, and standard deviation of ICA decreased with arrangement (Figure 8). However far from interface, formed structure was not the same to that of the interface. (Figure 9)

Figure 9. Sequence of ordered planes formed in the cell. Ratio of particle density between random phase and interface = 80%.)

When particle density in random phase decreased to 70% of ordered phase, ordered arrangement no longer grew up. Almost all particles were located randomly, however, some particles nearest the interface formed ordered plane similar to the interface. The arrangement at the nearest neighbour of the interface is considered to be formed clearly by the effect of interface.

These results suggest that ordered interface is effective, even if particle density of random phase is somewhat lower than that of ordered phase. In actual system, it is supposed that the collision energy affects on the particle is large and anisotropic in random phase than in ordered phase. Then particles in random phase are compressed toward the interface when they reached to the neighbour of the interface (for example, by depletion effect⁹ or flow of solvent). Under such a condition, arrangement will be occur even if particle density is somewhat low.

Figure 10. Variation of the size of ordered interface settled in the cell.

Effect of Cluster Size

Size of ordered cluster (fixed interface) was changed by setting the number of component particles at 54, 18, and 3 (Figure 10). The process of arrangement is expected to be affected by size of cluster.

When number of particles was 54 and 18, similar results were obtained. Standard deviation of ICA decreased with arrangement in the same way (Figure 11). But the effect of interface was not recognized, when the interface was composed only 3 particles (Figure 12). Standard deviations of ICA are approximately identical for each region. Ordered cluster composed of only a few particles is considered to be not enough to affect the process of arrangement.

In this simulation, we have not taken into consideration the effect of vibrational motion of particles in ordered phase. This motion should act to form regularly arranged phase from rather loosely arranged phase. Then the

Figure 11. The variation of standard deviation of interparticle contact angle with time as a function of the distance between interface and particles. Distance from interface: ●, 0—0.5; ○, 0.5—1.0; □, 1.0—1.5; △, 1.5—2.0. Interface is composed of 18 particles.

Figure 12. The variation of standard deviation of interparticle contact angle with time as a function of the distance between interface and particles. Distance from interface: ●, 0—0.5; ○, 0.5—1.0; □, 1.0—1.5; △, 1.5—2.0. Interface is composed of 3 particles.

small clusters compose of three particles for example, are in the critical state between ordered phase and random phase.

These results suggest that arrangement of particles is accelerated around larger cluster. So the ordered arrangement in microsphere system is considered to form by following mechanism. Initially ordered cluster with certain size is formed from random phase (nucleation). After nucleation, ordered structure is extended around the ordered cluster.

CONCLUSIONS

It is suggested that ordered structure of microspheres is extended around clusters with ordered structure, and that long range ordered

arrangement observed in solid state is formed as the result of this effect.

Arrangement of particles is accelerated, as ordered cluster (center of arrangement) becomes large.

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