

Available online at www.sciencedirect.com



Transactions of Nonferrous Metals Society of China

Trans. Nonferrous Met. Soc. China 18(2008) 421-425

www.csu.edu.cn/ysxb/

Effects of shear rates on radial distribution of different types of heavy particles in light media

LI Jing-sheng(李敬生), WANG Juan(王娟), SHEN Qin(沈琴), ZHENG Ning-ning(郑宁宁)

School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China

Received 31 May 2007; accepted 17 October 2007

Abstract: In order to study distribution properties of different types of heavy particles in light media and to link macro-properties of a system with its micro-structures, radial distribution functions(RDF) of partly charged metallic particles in uni- and bi-polar systems at various shear rates were investigated by Brownian dynamics simulation. The results are good in agreement qualitatively or quantitatively compared with ones in non-polar systems and other works. The investigation indicates that dispersibility of the particles in the uni-polar system of high ionic concentrations is the largest. Therefore, it is the most unfavored to grow into clusters for precipitation. The dispersibility in the bi-polar systems is less than that in uni-polar systems, but larger than that in non-polar systems. Furthermore, all the RDFs at the same shear rates in three systems approach a limit, which implies that a threshold value exists.

Key words: radial distribution function; heavy particle; microstructure; shear stress

1 Introduction

Microstructures and macroproperties of superfine particles, especially the superfine particles of metals and their compounds, are becoming interested areas and cause more investigations because of huge potential applied values and important scientific significance in nanometer materials, catalysis and environment protection. These investigations have dealt with micro-properties such as radial distribution functions[1], micro-structures at metallic solid/liquid interface in phase-changing process[2], micro- mechanism of precipitation processes and morphological features[3]. And these results supplied a good window, through which one can look into their microstructures and characteristic and into the relationships between macroscopic properties and the microstructures.

All these work, however, in spite of research on macro-properties or microstructures, usually only touched on systems of non-charged particles, and little attention has been paid on the systems of charged particles systematically. On the other hand, applications of a system constituting charged particles in a light medium are widely used. Microstructure and features of charged particles play an important role in floating dust recovery[4]. Microstructures and properties of charged particles have a large effect on extraction speed and product efficiency[5]. Charged metallic particles in electro-gilding solutions would affect surface polishing degree and quality of parts[6].

The aim of this work is to study effects of shear rate on microstructures and macro-properties in non-polar, uni-polar and bi-polar particle systems (definitions given below), and to search for the linkage between microstructures and macro-properties in metallic colloidal solution due to shear stresses executed.

2 Simulation

Langevin equation with an inertial term was chosen as the governing equation:

$$\begin{aligned} \frac{\mathrm{d}p}{\mathrm{d}t} &= -\nabla U - \xi (p - \gamma y \overline{x}) + R(t) \\ \frac{\mathrm{d}x}{\mathrm{d}t} &= \frac{p}{m} \end{aligned} \tag{1}$$

Foundation item: Project(50474037) supported by the National Natural Science Foundation of China; Project(BK2006078) supported by the Department of Science and Technology of Jiangsu Province, China

Corresponding author: LI Jing-sheng; Tel: +86-13646101959; E-mail: jli5154@ujs.edu.cn

The meanings of all parameters and the conditions in Eqn.(1) can refer to Ref.[7]. Further, as the density differences in colloidal particles and their media are few in many systems, so the inertial term is usually omitted. However, the density differences of metallic superfine particles and their aqueous solution in our systems are very large, so the inertial term must be remained.

Characteristics and properties of superfine particles in a medium differ from different systems. For non-charged particles, interaction potential energy can be conveniently represented by Lennard-Jones potential. For charged particles, however, electrostatic interaction should be taken into account:

$$U_{ij} = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 \varepsilon_1 r_{ij}}$$
(2)

Again, the meanings of all parameters and the conditions in Eqn.(2) can refer to Ref.[8]. X-ray absorption fine structure shows that this potential is reliable in describing metallic ions such as Ni^{2+} in aqueous solution[9].

For safety, a wide margin of a reduced cut off distance $r^*=4.0$ was used in all the three systems. For Ni^{2+} , the distance is about 7.0–8.0 nm. This distance was proved to be sufficient both experimentally and computationally, and Ewald sum method was used in bi-polar systems. In uni-polar system (again, all systems definition given below), a completely different modified model was used[10]. Reduced temperature of all simulations is $T^*=0.695$. This temperature is equivalent to operate in a dilute solution at ambient temperature. The estimated method comes from Ref.[11]. Reduced density is $\rho^*=0.2$, and time step is 0.002 ns. 500 particles in simulations are fixed at a FCC lattice at the start. Periodic boundary conditions and canonical ensemble are used. According to computational conditions, appropriate shear rates are executed and/or metallic superfine particles are charged. Each particle is simple point charge without distribution. A simulation is run for at least 10 000 time steps to guarantee a stable or equilibrium states (average energy fluctuation $\leq 3\%$ without shear rates or $\leq 5\%$ with shear rates); then the simulation proceeds another 10 000 time steps and data are stored every 100 time steps for analysis. Numerical method of Langevin equation, insertion of shear rates and other computational details such as cluster definition, can refer to Refs.[7, 12].

All the parameters in these simulations are reduced ones (dimensionless). The relations between reduced and normal parameters can refer to appendix B in Ref.[13]. Programme validations, and simulation conditions can refer to Ref.[14]. In this work, non-polar systems refer to the systems containing non-charged particles; bi-polar systems to the ones containing charged particles with the equal number of positive and negative ions; and unipolar systems to the ones containing the particles either positive or negative charge. Two ionic concentrations were taken in the uni-polar systems. If a system of 50 positive (or negative) particles is charged, equivalent to 10% of ionic concentration, it is called ep10; and if a system of 100 positive (or negative) particles is charged, equivalent to 20% ionic concentration, it is called ep20. The two ionic concentrations were computed separately in uni-polar system to examine the effects of ionic concentration on properties of the systems.

3 Results and discussion

3.1 Comparison of RDFs with different charging concentrations in uni-polar systems

Fig.1 shows comparison of RDFs of different ionic concentrations at different shear rates in a uni-polar system. It can be seen from Fig.1 that radial distribution functions $g(r^*)$ in the system with high concentration (ep20) are always lower than those in the system with low concentration (ep10), which implies that local structures in the higher concentration systems are more homogeneous than those in the low concentration system. For example, $g(r^*)$ that indicates heterogeneity of local structures with low (ep10) and high (ep20) concentrations at $\dot{\gamma} = 3.0$ are 11.26 and 8.51 respectively. When shear rate increases to 5.0, the former is larger by 0.2 than the latter. When shear rate increases to 7.0, the former is still larger by 0.06 than the latter. These facts indicate that the local structures in the low (ep10) concentration systems are more inhomogeneous than those in high concentration system, and the local structures in the high (ep20) concentration systems seem "solider" than those in low concentration system as $g(r^*)$



Fig.1 Comparison of radial distribution functions of different concentration in uni-polar systems

for ep20 is more insensitive to damage by increasing shear rates. In particular, $g(r^*)$ in the lower concentration system decreases more remarkably than their counterparts in the high concentration systems, and this eventually leads to roughly same $g(r^*)$ in the both systems. This corroborates that larger repulsive forces from more sign-like particles will drop off the trend of particle aggregation, and in turn, the decrease of this trend will make original inhomogeneous structures in the systems more homogeneous.

3.2 Comparison of RDFs in different systems

Fig.2 shows comparison of RDFs in a uni-polar system with those in a non-polar system. It can be seen that the radial distribution functions $g(r^*)$ at all shear rates in uni-polar systems are lower than their counterparts in non-polar systems with different discrepancies of 1.13, 0.25 and 0.04 respectively. The decrease is the most remarkable for the first peak at $\dot{\gamma}$ =3.0, lower by about 12%. This is due to the repulsive forces between the sign-like particles in the systems, in which counteract part attractive forces are produced by Lennard-Jones potential. Particles under the repulsive forces are obviously unfavorable to go closely and to aggregate, therefore the height of $g(r^*)$ falls off. This indicates that aggregating ability in the uni-polar systems is poorer than that in the non-polar systems; however, homogeneousibility and stability of the former are better than those of the latter. Again, the differences of $g(r^*)$ with increasing shear rate become smaller and smaller. This may imply that although higher $g(r^*)$ in the non-polar systems would lead to larger clusters, combining intensity of the particles in these systems is weaker, which leads the discrepancies of decrease in $g(r^*)$ almost gradually to vanish.



Fig.2 Comparison of radial distribution functions in uni- and non-polar systems

Fig.3 and Fig.4 show comparison of RDFs in bi-polar systems with those in non-polar and uni-polar systems respectively. Fig.3 shows that particles are likely

to gather at shear rate $\dot{\gamma} = 3.0$ at the first coordination shell of radial distribution in non-polar systems compared with their counterparts in bi-polar systems. However, the aggregated clusters under weak interaction forces are loose. As shear rates increase, the altitude differences of the $g(r^*)$ in non- and bi-polar systems decrease gradually. For example, when shear rate $\dot{\gamma} = 3.0$, the altitude difference is 1.93; while $\dot{\gamma}$ =5.0, the difference drops to 0; whereas $\dot{\gamma}$ =7.0, the difference even becomes -0.02. This again implies that the particles in the first coordination shell in bi-polar systems are on average bound stronger than those in non-polar systems, therefore the solid bound particles are able to resist large damage of shear rates to the first coordination shell. Though the more particles are aggregated in the first shell in non-polar systems, the combination intensity of the particles in non-polar systems is not as solid as that in the bi-polar system from statistical point of view, finally the RDFs in the both systems approach to nearly the same. Fig.4 shows comparison of RDFs in bi-polar systems with those in uni-polar systems (ep10). Good stable degree of combination of particles at different shear



Fig.3 Comparison of radial distribution functions at different shear rates in bi- and non-polar systems



Fig.4 Comparison of radial distribution functions at different shear rates in bi- and uni-polar systems

rates in bipolar systems can be seen more clearly. The highest peak value of $g(r^*)$ at $\dot{\gamma} = 3.0$ in uni-polar system is 3.55 higher than its counterpart in bi-polar system. However, while shear rate is 5.0, peak value of the $g(r^*)$ in the bi-polar system is 0.05 higher than that in the uni-polar system, whereas at shear rate $\dot{\gamma} = 7.0$, the altitude value continues to increase to 0.1. Again this means that the combination intensity of the particles in the bi-polar systems is much stronger than that in the uni-polar systems.

To sum up, the particles in non-polar systems are the easiest to gather, but their combination intensity is the weakest. Contrarily, particles in high ionic concentration systems are hardest to aggregate. However, the solid degree of the clusters in such systems is the largest. This leads to a threshold existed in all systems, and all of the RDFs approach the threshold with shear rates increasing. From the practical point of view, this is a limitation of stirring operation. Beyond this limit, mixing function by further increasing stirring operation is little.

3.3 Comparison of RDFs with different type particles in system

Fig.5 shows comparison of RDFs of different type particles, i.e. non-polar particles (uncharged particles) and the particles with positive and negative ions at $\dot{\gamma}$ =5.0 in bi-polar system. The response of RDFs $g_n(r^*)$ of uncharged particles in the system to shear rates is as exactly the same as usual. The highest peak of $g_n(r^*)$ is at the top of reduced distance $r^*=1.0$; the sub-peak is at the top of $r^*=2.0$; the $g(r^*)$ gradually decreases with distance r^* , etc. $g_t(r^*)$ is total RDFs of all particles. However, there are at least two points to emphasizing: one is that there is a "skew" (as the arrowhead points in Fig.5) on the left side of $g_t(r^*)$ raising stage; another is that the subpeak of the $g_t(r^*)$ is at the top biased left, instead of the exactly top as usual. Both phenomena are probably caused by the positive and negative ions in the system, because the position of the "skew" on $g_t(r^*)$ on X-axis is exactly the same place as that of the first peak of positive ion $g_{+}(r^{*})$ and negative ion $g_{-}(r^{*})$ below. Further, the position of "the skew" being less than one diameter of a particle (i.e. $r^* < 1.0$) might also means that some particles in the system have "closed combination" or "reaction" from chemical reaction point of view. RDFs $g_{+}(r^{*})$ and $g_{-}(r^{*})$ of positive and negative ions are under the $g_n(r^*)$ of the non-polar particles, and both curves are roughly equal with little fluctuations. The heights of $g_{+}(r^{*})$ and $g_{-}(r^{*})$ are roughly level, which implies that the ions with sign-like particles make their distances on average increase as much as possible, i.e. to make the particles more homogeneous (repulsive action). Since the peaks of $g_{+}(r^{*})$ and $g_{-}(r^{*})$ shift to the left, the curve heights at the distance $r^*=1.0$ even become low, and this should be a natural result that many particles gathered together at $r^* < 10$, since this event makes rare particles go to the left from the normal distance compared with $g_n(r^*)$ at this region in non-polar system. Compared with Ref.[15], there are at least three points keeping in a good agreement. Firstly, the $g(r^*)$ between ions-molecules raises the highest peak when distance between particles is closed to $r^*=1.0$. Our results of $g_t(r^*)$ for total particles (a mixture of all ions and neutral particles) in Fig.5 even better than that of Ref.[19] and more closer to CAILLOL et al's[16]. CAILLOL et al's results come from completely different ways. Secondly, the sub-peak of RDFs in Refs.[15–16] locates above the reduced distance $r^*=2.0$ exactly, which is in a good agreement with our results of non-polar particle system. i.e. $g_n(r^*)$ in Fig5. RDFs of positive and negative ions in Fig.5 in this investigation keep again the same trend as Fig.1 and Fig.2 in Refs.[19-20] in that both sub-peaks locate the position at above distance $r^* < 2.0$.



Fig.5 Comparison of radial distribution functions of different type particles at $\dot{\gamma}$ =5.0 in bi-polar system

4 Conclusions

1) The particles at high ionic concentrations in uni-polar systems are the most unfavorable to aggregate compared with those in bi-polar and non-polar systems. Furthermore, the higher the concentrations of uni-polar charged ions are, the smaller the clusters. Particles in uni-polar systems are suitable to suspend and uneasy to precipitate.

2) Shear rates lead the structures of colloidal solution to be more homogeneous in all systems considered, and the larger the shear rates are, the more homogeneous the structures are.

3) Structures in all different systems approach to be the same. This is the limit of stirring operation, and beyond this limit, the function of stirring operation is little.

References

- YU Wong, ANDREW C T. Heterogeneous aggregation in binary colloidal alloys [J]. Physica A: Statistical Mechanics and its Applications, 2002, 312: 50–58.
- [2] YANG Xi-yuan, HU Wang-yu, YUAN Xiao-Jian. Molecular dynamics simulation of melting behavior of (001) plane of niobium and tungsten [J]. The Chinese Journal of Nonferrous Metals, 2006, 16(7): 1171–1176. (in Chinese)
- [3] LU Yan-li, CHEN Zheng, LI Yong-shang, WANG Yong-xin. Microscopic phase-field simulation coupled with elastic strain energy for precipitation process of Ni-Cr-Al alloys with low Al content [J]. Trans Nonferrous Metals Soc China, 2007, 17(1): 64–71.
- [4] ADACHI M, KONSAKA Y, OKUYAMA K. Unipolar and bipolar diffusion charging of ultrafine aerosol particles [J]. Aerosol Sci, 1985, 16: 109–123.
- [5] PESIC B, ZHOU Tai-li. Application of ultrasound in extractive metallurgy: Sonochemical extraction of nickel [J]. Metallur Trans B, 1992, 23B(1): 13–22.
- [6] XU Sheng-ming, ZHANG Chuan-fu, WU Yan-jun. Application of ultrasound in the metallic solvent extraction and ion exchange [J]. Rare Metals and Cemented Carbides, 1995, T121: 47–51.
- [7] LI Jing-sheng, RODGER P M, Characteristic of colloidal aggregates with weakly bound potential under shear [J]. Acta Physica-Chimica Sinica, 1997, 13(1): 20–35.

- [8] CHIALVA A A, SIMONSON J M. The structure of concentrated NiCl₂ aqueous solutions: What is molecular simulation revealing about the neutron scattering methodology? [J]. Mol Phys, 2002, 100(14): 2307–2315.
- [9] WALLEN S L, PALMER B J, FULTON J L J. The ion pairing hydration structure of Ni in supercritical water at 425 °C determined by X-ray absorption fine structure and molecular dynamics studies [J]. Chem Phys, 1998, 108(10): 4039–4046.
- [10] PARK H, KIM S, CHANG H. Brownian dynamic simulation for the aggregation of charged particles [J]. Aerosol Science, 2001, 32: 1369–1388.
- [11] BIRD R B, STEWARD W E, LIGHTFOOT E N. Transport phenomena [M]. 2nd Ed. New York: John Wiley & Sons Inc , 2002.
- [12] LAN Xin-zhe, LI Jing-sheng, JIN Zhi-hao, ZHANG Jian. Brownian dynamics simulation on nano-meter gold colloids and experimental study [J]. Journal of Chinese Rare Earth Metals, 2002, 20(S): 465–468.
- [13] NICOLAS J J, GUBBINS K E, STREETT W B. Equation of state for the Lennard-Jones fluid [J]. Mol Phys, 1979, 37: 1429–1454.
- [14] LI Jing-sheng, WANG Juan, SHEN Qin. Clustering properties of partly charged superfine particles in a light medium [J]. Chi Chem Letts, 2007, 18: 1419–1422.
- [15] WU Jian-zhong, LU Jiu-fang, LI Yi-gui. Perturbation theory of electrolyte solution [J]. J Chem Ind and Enging, 1994, 45(2): 168–175.
- [16] CAILLO J M, LEVESQUE D, WEIS J J. Monte Carlo simulation of an ion-dipole mixture [J]. Mol Phys, 1990, 69(1): 199–208.

(Edited by LI Xiang-qun)