

Viscosity and thermal conductivity of copper oxide nanofluid dispersed in ethylene glycol

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(Received March 22, 2005; final revision received April 11, 2005)

Abstract

Nanofluid is a novel heat transfer fluid prepared by dispersing nanometer-sized solid particles in traditional heat transfer fluid to increase thermal conductivity and heat transfer performance. In this research we have considered the rheological properties of nanofluids made of CuO particles of 10-30 nm in length and ethylene glycol in conjunction with the thermal conductivity enhancement. When examined using TEM, individual CuO particles have the shape of prolate spheroid of the aspect ratio of 3 and most of the particles are under aggregated states even after sonication for a prolonged period. From the rheological property it has been found that the volume fraction at the dilute limit is 0.002, which is much smaller than the value based on the shape and size of individual particles due to aggregation of particles. At the semi-dilute regime, the zero shear viscosity follows the Doi-Edwards theory on rodlike particles. The thermal conductivity measurement shows that substantial enhancement in thermal conductivity with respect to particle concentration is attainable only when particle concentration is below the dilute limit.

Keywords : nanofluid, Brownian motion, thermal conductivity

1. Introduction

Nanofluid is a novel heat transfer fluid prepared by dispersing nanometer-sized solid particles in traditional heat transfer fluid such as water or ethylene glycol to increase thermal conductivity and therefore heat transfer performance. For example, when 0.3 volume percent of copper nano-particles are dispersed in ethylene glycol, one can observe about 40% of increase in thermal conductivity (Eastman and Choi, 1995). Metal oxides such as aluminum oxide or titanium oxide are also feasible even though the amount of heat transfer increase is not as large as metal particles (Masuda *et al.*, 1993). The effectiveness of heat transfer enhancement is known to be dependent on the amount of dispersed particles, material type, particle shape, and so on. It is expected that nanofluid can be utilized in airplanes, cars, micro machines in MEMS, micro reactors among others. Before the introduction of nanofluid, it was expected that heat transfer could be enhanced by dispersing micron-sized particles. But the fluid with micron-sized particles caused problems due to sedimentation and clogging (Xuan and Li, 2000). Most of all, the fluid with micron-sized particles was found to be not efficient enough. Since the concept of nanofluid has been first introduced by East-

man and Choi (1995), there have been many efforts to understand the mechanism of heat transfer enhancement together with experimental measurements of the thermal conductivity of nanofluids and the methods of utilization of nanofluids.

However there has been no established mechanism for the heat transfer enhancement. The reason may arise from the difficulty caused by the fact that the heat-transfer between the base fluid and particles occurs while the particles are in random Brownian motion. Also, depending on the flow condition and chemical nature of particles, dispersion state can be different. Xuan and Roetzel (2000) suggested a mechanism by assuming that nanofluid behaves similarly to common solid suspensions in liquid. Koblinski *et al.* (2002) argued that the heat transfer increases due to the combined effect of Brownian motion of nano-particles, formation of liquid-solid interface, large conductivity of particle itself and clustering of nano-particles.

There have been some reports on the rheological behavior of suspension of nano-particles. Xiao-Bing *et al.* (2001) reported the viscosity of nanofluid by using the molecular dynamic simulation and kinetic theory. Zaman *et al.* (2002) and Zaman (2000) reported on the rheological properties and surface charge of polyethylene-coated silicone oxide particles. Chandmular (2000) reported on the rheological properties of aqueous solution of titanium oxide under the

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presence of cellulose. Aoki *et al.* (2003) considered the carbon black dispersed system. Bently (1984) reported the dispersion stability and rheological properties of a latex system with adsorbed copolymers. However the particles used in those researches were low k materials and heat transfer experiments were not performed hence we cannot directly apply their results to nanofluid systems.

Until now, there have been few researches on the characteristics of dispersion and rheological properties of nanofluids. Since nanofluids are expected to be used under flow conditions and the flow of suspension is sometimes drastically different from that of most common heat transfer fluids that have Newtonian characteristics, it is essential to have the rheological properties of nanofluid to use practically. Also, to understand the mechanism of heat transfer enhancement it is crucial to have the ideas on the fluid-particle and particle-particle interactions within the fluid. Since the rheological properties can provide us with the knowledge on the microstructure under both static and dynamic conditions, the study on the rheological properties of nanofluid may reveal the route to understand the mechanism of heat transfer enhancement, and hence the design of nano-particles for the maximum heat transfer enhancement. In this study, we investigated the thermal conductivity and rheological properties of copper oxide nanofluid dispersed in ethylene glycol.

2. Experimental

2.1. Materials and dispersion of nano-particles in base fluid

As the nano-particle copper oxide (CuO, Integran Technologies Inc., Canada) was used. The CuO particles have



Fig. 1. TEM image of CuO particles. Before dispersed in liquid, particles are strongly aggregated.

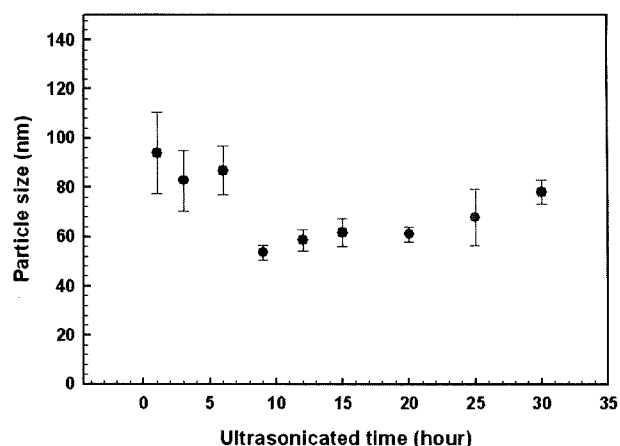


Fig. 2. Average particle size of CuO particles after sonication. Particles are dispersed in ethylene glycol. The average diameter has the minimum value when the duration of sonication is 9 hours.

the diameter of 10-30 nm and the average diameter of the particles is 12 nm. The shape is rod-like as shown in Fig. 1. The exact aspect ratio is not known, but from the TEM image after dispersion, it is estimated to be approximately 3. CuO has the density of $6,000 \text{ kg/m}^3$. As the base fluid reagent grade ethylene glycol was used. When nano-particles were poured into the base fluid, particles sedimented within several minutes because the particles remain within the clusters without being dispersed. To disperse particles sonication was used with an ultrasound generator (20 kHz, 100W). It was found that if the duration of sonication is too long particles get coalesced again. To determine the optimum duration of sonication, we varied the duration from 1 to 30 hours and measured the average size of particles as shown in Fig. 2. From the figure we can conclude that the optimum duration is 9 hours and the average value is approximately 60 nm. This value is about 5 times larger than the individual particle and hence the dispersion is not completed yet. The average particle size, hence the status of dispersion is found to be independent of particle volume fraction when the volume fraction is less than 0.05 which is thought to be close to the maximum amount of solid content as useful nanofluid. In Fig. 3, a TEM image is shown for the nanofluid sonicated for 9 hours. The image shows that CuO particles are still connected even though they are separated from the clusters as shown in Fig. 1. The smallest average diameter is also confirmed by the largest absolute value in zeta potential based on the reasoning that the larger value indicates that the particles are better dispersed (See Fig. 4). Here we used the dynamic light scattering technique with ELS-8000 (Otsuka Co.). To check the stability of the nanofluid we measure the average particle size after waiting 100 days and find that the average sizes remain virtually the same as shown in Fig. 5. The



Fig. 3. TEM image of CuO particles dispersed in ethylene glycol after 9 hours. Particles are still in an aggregated state. The average aspect ratio is approximately 3.

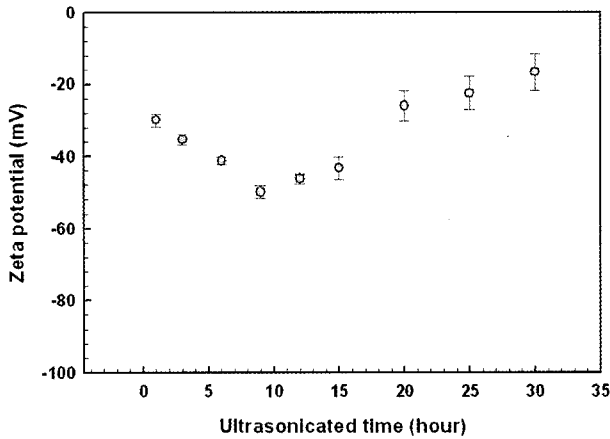


Fig. 4. The effect of sonication on zeta potential value of CuO particles. Particles are dispersed in ethylene glycol. Zeta potential has the minimum value when duration of sonication is 9 hours, hence the dispersion is regarded as the best under this condition.

sedimentation characteristic was examined using TURBISCAN Lab which is a commercially available sedimentation tester. In Fig. 6, typical TURBISCAN Lab results are compared for nanofluids sonicated for 1 and 9 hours. The nanofluid sonicated for 9 hours has lower initial transmission and less change in the amount of back scattering than the one sonicated for 1 hour. This means that the nanofluid sonicated for 9 hours is more resistant against

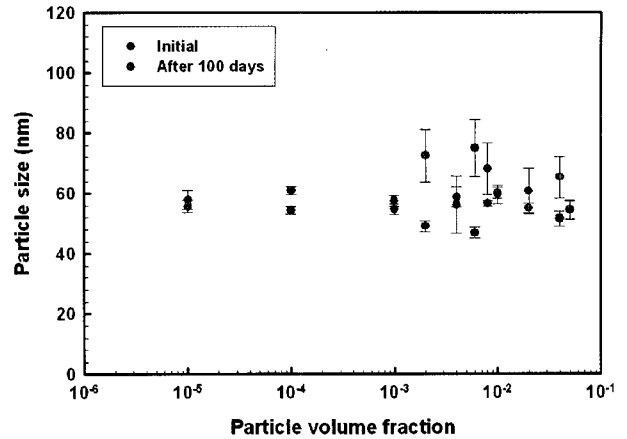


Fig. 5. Change in the average particle size. The average particle size remains the same after the long time standing of 100 days regardless of particle volume fraction. Hence the nanofluid is regarded as stable against aggregation.

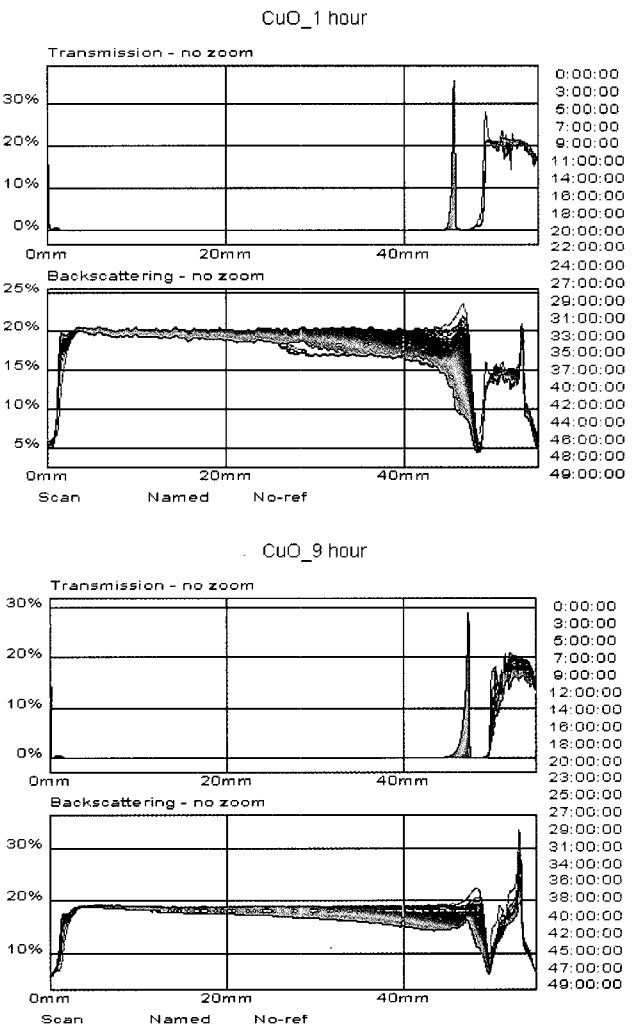


Fig. 6. TURBISCAN Lab data after 1 hr (above) and 9 hrs (below).

sedimentation hence is more stable. From the above independent studies we concluded that CuO nanofluid sonicated for 9 hours is the best dispersed and most stable. In the following we studied the rheological and thermal properties only for this case.

2.2. Measurement of rheological properties

Rheological properties were measured using an ARES-LS (Rheometrics Inc.) with the Couette fixture and AR2000 (TA Instrument) with an acrylic parallel plate. The inner and outer diameters of the Couette fixture are 32 and 34 mm, respectively and the height is 32 mm. The diameter of the acrylic plate is 60 mm and the lower plate is the constant temperature peltier with a sufficiently larger diameter compared with the acrylic plate. All the measurements were done at 298 K. To measure the zero shear viscosity, a creep test was used with the AR2000 (A stress rheometer). Steady rate-sweep tests were performed between 0.01 and 100 s⁻¹ in shear rate.

2.3. Measurement of thermal conductivity

The thermal conductivity of nanofluid was measured using the transient hot-wire method used in most studies where the temperature increase of the hot-wire (platinum in this experiment) is related to the thermal conductivity k of fluid as follows (Nagasaka and Nagashima, 1981):

$$k = \frac{q}{4\pi l} \frac{d \ln \Delta T}{d \ln t} \quad (1)$$

In the above equation, q is heat generation per unit length, ΔT is temperature increase, t is time. The temperature of the platinum hot-wire is estimated from the following relationship suggested by Bently (1984):

$$R = R_0[1 + \alpha(T - 273.15) + \beta(T - 273.15)^2] \quad (2)$$

where $\alpha = 3.9092 \times 10^{-3} \text{ K}^{-1}$ and $\beta = -5.9170 \times 10^{-7} \text{ K}^{-2}$ and T is in K. The measuring cell has a dimension of 30 mm in diameter and 70 mm in height. The platinum hot wire has the diameter of 25 micrometer and the length of 50 mm. The cell was immersed in a bath maintained at 298 K. To avoid the effect of natural convection and the initial disturbances, data were collected only between 100 and 300 ms.

3. Viscosity of nanofluid

Shear viscosities of nanofluid were measured with the ARES-LS in rate-sweep mode over the shear-rate range 0.01-100 s⁻¹. In determining the zero-shear viscosity of less viscous nano-fluid we used an AR2000 rheometer in the creep test mode. In Fig. 7, zero-shear viscosities of nanofluid are shown with the solid content between 10⁻⁵ and 0.05. Since the particles have a shape of prolate-spheroids

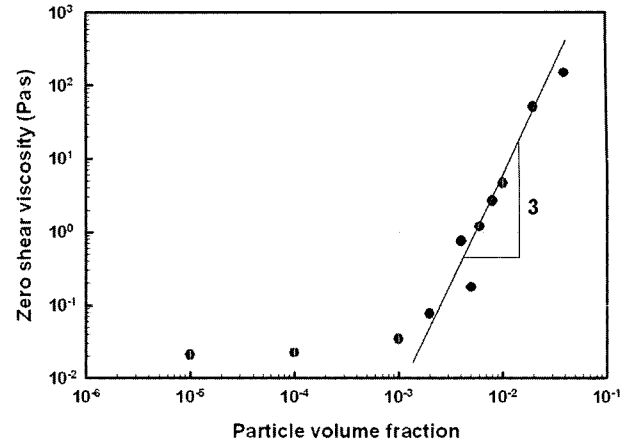


Fig. 7. Zero shear viscosity as a function of particle volume fraction. The zero shear viscosity changes abruptly when particle volume fraction becomes larger than 0.002, hence it is regarded as the dilute limit. When particle volume fraction is larger than the critical value the slope is 3. This value is in quantitative agreement with the Doi-Edwards theory in the semidilute solution of rodlike particles.

with an aspect ratio of approximately 3, the intrinsic zero shear viscosity is expected to have about 5. This means that the critical particle volume fraction ϕ at the dilute limit is 0.2. However the zero-shear viscosity value at $\phi = 0.2$ is expected to be far larger than twice the solvent viscosity as shown in Fig. 7. This discrepancy is caused by the coalescence of particles, which results in the increase in the apparent aspect ratio. From the value at which the viscosity doubles the solvent value (From the figure one can notice that it occurs at $\phi \approx 0.002$), it is estimated that the intrinsic viscosity is about 500 and the apparent aspect ratio is estimated to be 90 using the relationship given in Larson (1999) as follows when the aspect ratio p is sufficiently large:

$$[\eta]_0 = \frac{4p^2}{15 \ln(p)} \quad (3)$$

The extremely larger value of aspect ratio than the value for an individual particle is already discussed during the explaining the result in Fig. 2. In Fig. 7 we can notice that the slope of zero shear viscosity vs. ϕ is very close to 3 when ϕ is larger than the dilute limit of 0.002, therefore the suspension is considered to be semi-dilute region if particle concentration is larger than 0.002. The slope value of 3 is in quantitative agreement with Doi-Edwards or Marrucci-Grizzutti theory on semi-dilute regime of rod suspension (Larson, 1999). Therefore the CuO nanofluid behaves as a semi-dilute rodlike particle suspension for the concentration range up to 0.05. The same behavior of $\eta_0 \propto \phi^3$ has been also reported by Mead and Larson with semi-dilute solutions of poly(γ -benzyl-L-glutamate) (PBLG; molecular weight 231,000) which has a rodlike shape (Larson, 1999).

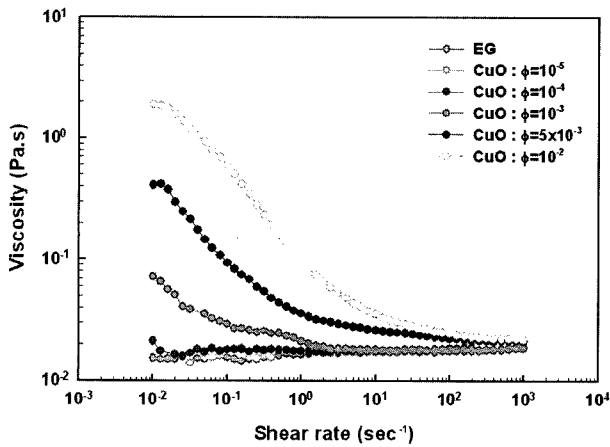


Fig. 8. Shear dependent viscosities of nanofluids. The fluids show very strong shear thinning reflecting the high aspect ratio.

When particle concentration is over 5 to 10%, due to the excluded volume effect (so called rod jamming) very high zero-shear viscosities are expected. But this range is out of interest as nanofluids.

The viscosities of nanofluid have been found to be very shear thinning as shown in Fig. 8 and the infinite shear viscosities become almost the same as the solvent viscosity. This is also predicted for the suspension of rodlike particles with large aspect ratio. When the aspect ratio is large the intrinsic viscosity asymptotes to (Larson, 1999).

$$[\eta]_{\infty} = \frac{1.18}{p} \quad (4)$$

In this case this value is less than 0.01, and hence the contribution is negligible. We have seen that the viscosities of CuO-ethylene glycol nanofluid show that particles exist in aggregated form. It has a strong effect on the thermal conductivity of nanofluid as discussed below.

4. Thermal conductivity of CuO-Ethylene Glycol nanofluid

The thermal conductivity of nanofluid was measured by the hot-wire method. To exclude the effect of natural convection, data were collected only from 100-300 ms. As expected the thermal conductivity of nanofluid increases as concentration of particles increases as shown in Fig. 9. Even at a very low concentration of 0.001, about 2.6% increase is observed which is very high compared to the volume fraction of particles. Therefore the effectiveness of adding particles is sufficiently large when the volume fraction is less than 0.001. However, if volume fraction is larger than 0.002, the increase is not conspicuous as in the case of low volume fraction. According to Hamilton-Crosser theory (1962) on the effective thermal conductivity

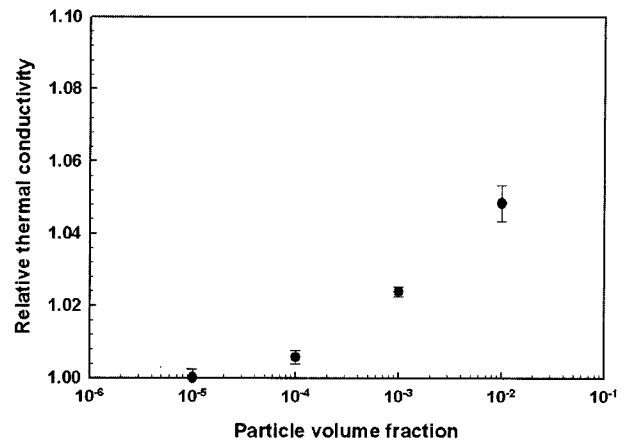


Fig. 9. Relative thermal conductivities of CuO-ethylene glycol nanofluids.

of two-phase material k_{eff} , the ratio of thermal conductivities of nanofluid and base fluid (ethylene glycol in the present study) is given as follows:

$$\frac{k_{eff}}{k_f} = \frac{\beta + (n-1) - (n-1)\phi(1-\beta)}{\beta + (n-1) + \phi(1-\beta)} \quad (5)$$

where k_f is the thermal conductivity of base fluid, n is $3/\Psi$ (Ψ is sphericity), β is the ratio of thermal conductivities of solid particle and base fluid and ϕ is volume fraction. In the present study we have no data for n for aggregated particles. An alternative expression for calculating the effective thermal conductivity of solid-liquid mixtures was introduced by Wasp (1977)

$$\frac{k_{eff}}{k_f} = \frac{\beta + 2 - 2\phi(1-\beta)}{\beta + 2 + \phi(1-\beta)} \quad (6)$$

According to this theory, the percent increase in thermal conductivity when particle loading is 1% is 3%. In the present experiment 6% increase is observed. Therefore there is some additional increase in thermal conductivity. However the increase is smaller than the values reported in the literature for most nanofluids. There are two major differences between the present research and the previous ones. One difference is the thermal conductivity of the particle. The thermal conductivity of CuO particles is 20 W/mK that is much lower than the value for metallic Cu of 400 W/mK. Therefore the heat transfer enhancement may not be large compared to metallic Cu based nanofluid. Another difference is the microstructure of particles. When particle concentration is less than the dilute limit, particles move and rotate freely, and in this case the increase in thermal conductivity is very large compared to the value determined by Eqn. (6) which is based on pure conduction. Such an increase is already seen in the above. If particle concentration is in the semi-dilute region, particles cannot move or rotate freely, and hence the heat transfer enhancement should be limited.

5. Concluding remarks

In this research we have considered the rheological properties of CuO-based nanofluid in conjunction with the thermal conductivity enhancement. Individual CuO particles have the shape of prolate spheroids and most of the particles are under aggregated states. From the rheological property it has been found that the volume fraction at the dilute limit is 0.002, which is much smaller than the value based on the shape of individual particles due to the aggregation of particles. The result shows that substantial enhancement in thermal conductivity is attainable only when particle concentration is below the dilute limit.

It is well known that nano-sized metal powder is dangerous to handle due to flammability. Also metal powders are susceptible to sedimentation due to large difference in density. The present result shows that metal oxides can be promising candidates as dispersed particles in nanofluid if aggregation can be minimized. In the present study due to aggregation the increase is only a few percents. But the present study shed some lights on the mechanism of heat transfer enhancement. If rotational Brownian motion is geometrically restricted, heat transfer cannot be increased. Since the motion of particles is known at least statistically, we may predict the amount of heat transfer enhancement. But this is out of scope of the present journal and hence is omitted here. The present study suggests that, to be an efficient nanofluid, the particles should have a spherical shape to have a higher critical dilute limit. It may be also feasible to use a prolate spheroid with a small aspect ratio to have both rotational and translational Brownian motions. But prolate spheroids with a large aspect ratio should be avoided not to become a semidilute solution with a small addition of particles.

Acknowledgment

The authors wish to acknowledge the financial support from the Applied Rheology Center, Korea University (ERC supported by KOSEF).

References

- Aoki, Y., 2003, Rheology of carbon black suspensions. 1. Three types of viscoelastic behavior, *Rheol. Acta* **42**, 209-216.
- Bentley, J.P., 1984, Temperature Sensor Characteristics and Measurement System Design, *J. Phys. E: Sci. Instrum.* **17**, 430-43.
- Chandramalar, A.V.M., 2000, Flow behaviour of titanium dioxide dispersions in the presence of 2-hydroxyethyl cellulose. *J. Colloid Polym. Sci.* **278**, 485-489.
- Eastman, J. and S. Choi, 1995, Anomalous Increased Effective Thermal Conductivities of Ethylene Glycol-Based Nanofluids, *Applied Physics Letters* **78**, 718-720.
- Hamilton, R.L. and O.K. Crosser, 1962, Thermal conductivity of heterogeneous two-component, *I&EC Fund.* **1**, 187-191.
- Kebllinski, P., S.R. Phillpot, S. Choi and J.A. Eastman, 2002, Mechanism of heat flow in suspensions of nano-sized particles (nanofluids), *J. Heat and Mass Transfer* **45**, 855-863.
- Larson, R., 1999, The structure and rheology of complex fluids, Oxford Univ. Press, New York.
- Masuda, H., A. Ebata, K. Teramae and N. Hishinuma, 1993, Alternation of thermal conductivity and viscosity of liquid by dispersing ultra-fine particles (dispersion of $-Al_2O_3$, SiO_2 and TiO_2 ultra-fine particles), *Netsu Bussei(Japan)* **4**, 227-233.
- Nagasaka, Y. and A. Nagashima, 1981, Absolute measurement of the thermal conductivity of electrically conducting liquids by the transient hot-wire method, *J. Phys. E: Sci. Instrum.* **14**, 1435-1439.
- Wasp, F.J., 1977, Solid-liquid flow slurry pipeline transportation, Trans. Tech. Pub., Berlin.
- Xiao-Bing, M. and A.T. Chwang, 2001, Nanofluid viscosity calculated by the kinetic theory and molecular dynamics simulations, MMC2001 Conference, 486.
- Xuan, Y. and Q. Li, 2000, Heat transfer enhancement of nanofluids, *J. Heat and Fluid Flow* **21**, 58-64.
- Xuan, Y. and W. Roetzel, 2000, Conceptions for heat transfer correlation of nanofluids, *J. Heat and Mass Transfer* **43**, 3701-3707.
- Zaman, A.A., 2000, Effect of polyethylene oxide on the viscosity of dispersions of charged silica particles : interplay between rheology, adsorption, and surface charge, *J. Colloid Polym. Sci.* **278**, 1187-1197.
- Zaman, A.A. and N. Delorme, 2002, Effect of polymer bridging on rheological properties of dispersions of charged silica particles in the presence of low-molecular weight physically adsorbed poly(ethylene oxide), *Rheol. Acta* **41**, 408-417.