Investigation of collective dynamics of solvent molecules in nanofluids by inelastic X-ray scattering

A highly efficient heat transfer medium could be realized by increasing the thermal conductivity of fluids. Many studies have been conducted on the fabrication of nanofluids, in which nanoparticles are dispersed homogenously into a medium. By adding a small amount of copper (Cu), silver (Ag), or alumina (Al_2O_3) nanoparticles, the thermal conductivities of water and ethylene glycol (EG) are increased by 20 to 40% [1]. These thermal conductivities exceeded the theoretical values, and it was deduced that nanoparticles affect solvent molecules in some way. Several hypotheses, such as Brownian motion, clustering, ballistic transport, and the creation of an inter-nanoparticle potential, have been proposed to explain the high thermal conductivity of nanofluids [2]. However, the effect of nanoparticles on a solvent has not yet been clarified. It is essential to understand solvent behavior in nanofluids to develop an efficient heat transfer medium.

A high-resolution inelastic X-ray scattering (IXS) method has been used to investigate the collective dynamics of many liquids, such as water, organic solvents, ionic liquids, and liquid metals [3]. By analyzing coherent scattering from a nanofluid, collective dynamics of solvent molecules can be clarified. The excitation of acoustic phonons is observed in collective dynamics in the low-momentum-transfer region (2–20 nm^{-1}). The dispersion relation between the excitation energy and momentum transfer gives a high-frequency sound velocity (HFSV) that reflects the thermal conductivity and structural relaxation of solvent molecules. This leads to the elucidation of the effect of nanoparticles on the heat transfer and molecular dynamics of nanofluids.

Cu nanoparticles (Cu NPs) with 50 nm average diameter are prepared by the polyol method [4] and dispersed in EG. For comparison with the effect of Cu NPs, a nanofluid of EG in which other NPs, such as Ag or Al_2O_3, are dispersed, is desired. However, an EG dispersion of other NPs is difficult to fabricate and is not readily available. Therefore, a nanofluid with Al_2O_3 NPs in water is examined for comparison. The thermal conductivities of Cu NPs/EG and Al_2O_3 NPs/water are measured experimentally. It is found that Cu NPs are more effective than Al_2O_3 NPs for increasing the thermal conductivity of the medium. The thermal conductivities of Cu NPs/EG samples with different Cu NP concentrations exceed the estimated values obtained from the Maxwell-Garnett theory. In contrast, the thermal conductivities of Al_2O_3 NPs/water samples are less than or equal to the estimated values [5].

IXS measurements at SPring-8 **BL35XU** were conducted at room temperature for both Cu NPs/EG and Al_2O_3 NPs/water samples with the NP concentrations listed in Table 1. Dynamic structure factors, $S(Q,\omega)$, are obtained by subtracting the scattering from an empty cell. The normalized IXS spectrum of IXS-EG-3 obtained at $Q = 5.58\ nm^{-1}$ is shown in Fig. 1. Generally, a large peak around 0 meV is from quasi-elastic scattering, and side or shoulder peaks are caused by inelastic excitation. A shoulder peak is observed at 4.7 meV in Fig. 1, although peaks from Cu NPs should be observed at much higher energy than those from the solvent. The damped harmonic oscillation (DHO) method was adopted to separate the side or shoulder peaks from the main quasi-elastic scattering peak. Twenty-four data sets per sample for different Q values were analyzed and the inelastic excitation energy at each peak was obtained.

Figure 2 shows the dispersion relation between the Q value and excitation energy for IXS-EG-3. The HFSV is calculated from the slope of the dispersion

Table 1. High-frequency sound velocity of nanofluids

Exp. No.	NPs	Solvent	Concentration (vol%)	HFSV (km/s)	Increase Ratio/conc.
IXS-EG-1	–	EG	0	2.31 ± 0.01	
IXS-EG-2	Cu	EG	0.5	2.34 ± 0.02	2.60
IXS-EG-3	Cu	EG	1.32	2.56±0.03	8.41
IXS-WA-4	–	water	0	2.72±0.03	
IXS-WA-5	Al_2O_3	water	2.53	2.76±0.02	0.49
IXS-WA-6	Al_2O_3	water	7.60	2.84±0.03	0.50

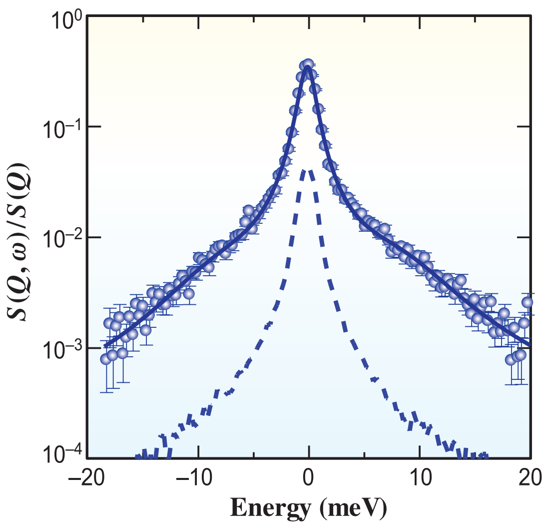

Fig. 1. Normalized inelastic X-ray scattering spectrum (IXS-EG-3, Q = 5.58 nm^{-1}). The solid line represents the DHO and Lorentzian fit including the convolution of the resolution function (dashed line).

relation. From Fig. 2, the HFSV is estimated to be 2.56 km/s for IXS-EG-3 by liner approximation using the least squares method. Since the HFSV of EG is 2.31 km/s, it is found that the existence of small amounts of Cu NPs increased the HFSV of EG 1.11-fold.

Table 1 summarizes the HFSVs of the samples. The HFSV increases with increasing amounts of Cu and Al_2O_3 NPs. The results indicate that the collective dynamics of EG and water is affected by the existence of NPs. The addition of 1.32 vol% Cu NPs brought about a 1.11-fold (2.56/2.31) increase in HFSV. On the other hand, in the case of the Al_2O_3/water system, the HFSV increases 1.04-fold (2.84/2.72) when 7.6 vol% Al_2O_3 NPs was added to water. To understand the effect of the NPs clearly, the relative increase is divided by the volume concentration of the NPs and the values are also listed in Table 1. It is clear from Table 1 that Cu NPs are over ten times more effective than Al_2O_3 NPs, although the solvent is different.

In summary, IXS measurements of two types of nanofluids (Cu NPs/EG, Al_2O_3 NPs/water) were conducted, and HFSVs of the series of samples were obtained. The effect of the NPs on the heat transfer and molecular dynamics of the medium of nanofluids was evaluated. The HSFV of EG was increased by 11% upon the addition of 1.32 vol% Cu NPs. It is suggested that the collective dynamics of EG is strongly affected by Cu NPs. In contrast, Al_2O_3 NPs had a limited effect on the dynamics of the solvent. It is found that the effect of Cu NPs on the solvent is significant.

The IXS method is a powerful tool for understanding the molecular behavior of a medium in nanofluids. The effect of NPs could be elucidated by the method, leading to the development of an efficient heat transfer medium.

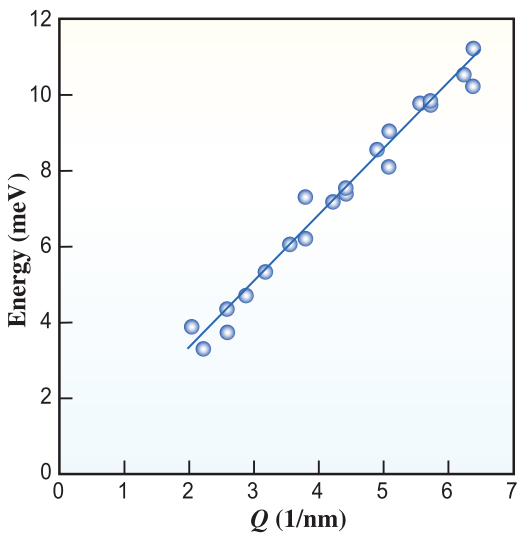

Fig. 2. Dispersion relation of the energy of the inelastic excitation (IXS-EG-3). The solid line is fitted by the least square method.

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