Magnetic Thermometer: Thermal effect on the Agglomeration of Magnetic Nanoparticles by Magnetic field

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Abstract. We have investigated the agglomeration of magnetite nanoparticles in the aqueous solution under magnetic field by measuring temporal change of magnetic weight. The magnetic weight corresponds to the force due to the magnetization of magnetic materials. Superparamagnetic magnetite nanoparticles are synthesized and used in this work. When the aqueous solution of magnetite nanoparticle is placed under magnetic field, the magnetic weight of the sample jumps instantaneously by Neel and Brown mechanisms and thereafter increases steadily following a stretched exponential function as the nanoparticles agglomerate, which results from the distribution of energy barriers involved in the dynamics. Thermal motions of nanoparticles in the agglomerate perturb the ordered structure of the agglomerate to reduce the magnetic weight. Fluctuation of the structural order of the agglomerate by temperature change is much faster than the formation of agglomerate and explained well with the Boltzmann distribution, which suggests that the magnetic weight of the agglomerate works as a magnetic thermometer.

1. Introduction
Magnetic nanoparticles have been studied extensively for their wide applications in various fields.[1-3] Magnetite nanoparticles have been used as magnetic recording medium as well as friction-reducing ferrofluid. Hyperthermia, drug delivery and MRI contrast enhancement are recent important examples of medical applications. Modifications of magnetic nanoparticle surface play important roles in the recycle of catalysts. Magnetic nanoparticles reveal very complicated behaviors under magnetic field.[4] Detailed knowledge about the magnetic nanoparticles under magnetic field will be instrumental in improving many application processes.

We have studied the dynamics of agglomeration of magnetite nanoparticles by monitoring the magnetic weight with an electronic balance. The magnetic weight \( W \) given by Eq. (1) corresponds to the vertical magnetic force \( F_z \) that the magnetic nanoparticles experience under magnetic field,

\[
W = F_z = \left[ VM(\nabla B) \right]_z. \tag{1}
\]

where \( V \) and \( M \) are the volume and the magnetization of the sample, and \( \nabla B \) is the magnetic field gradient. The magnetic weight can be measured easily as in the Gouy balance. The magnetite nanoparticles are superparamagnetic in the solution before applying the magnetic field. As the nanoparticles agglomerate and the ordered structure develops inside the agglomerate under magnetic field, the magnetization as well as the magnetic of the agglomerate weight is growing. The ordered structure of the agglomerate is assigned to ferromagnetic-like state. The magnetic weight of the agglomerate is sensitive to the temperature. Some particles of the agglomerate that do not contribute to the magnetic weight due to the
thermal motions are considered to be in the superparamagnetic-like state. The temperature effect on the magnetic weight of the agglomerate is explained well with the Boltzmann distribution between the superparamagnetic-like state and the ferromagnetic-like state of the agglomerate, which suggests that the magnetic weight of the agglomerate is a good indicator of temperature, that is, the magnetic thermometer.

2. Experimental
Figure 1 shows the experimental setup for monitoring the temporal change of the magnetic weight.[5] The magnetic field is applied in the direction parallel to the gravity with the NdFeB disc magnet of 2 cm diameter and 1 cm thick. The strength of the magnetic field can be varied by translating the magnet vertically and measured with a magnetometer. The magnetic field strength is in the order of a few tens T m$^{-1}$ which is regarded as the low gradient range.[1] The magnetic weight of the sample is recorded every minute and the laboratory temperature is also monitored every minute with a digital thermometer.

The aqueous solution of 1.5 wt % magnetite nanoparticle is used in this work. The magnetite nanoparticles are synthesized by following a well-known procedure.[6] Tetramethylammonium hydroxide is used as the surfactant for magnetite nanoparticles of ~11 nm diameter.[5] High concentration solution of the synthesized nanoparticles reveals the characteristic behaviors of ferrofluid under magnetic field.[4] The magnetite nanoparticles are stable to keep the superparamagnetic state in the aqueous solution for several months or longer.

3. Results and Discussion

3.1. Agglomeration of nanoparticles under magnetic field
Figure 2 shows the agglomeration of magnetite nanoparticle under magnetic field. The magnet of Figure 2 is smaller than the magnet used in the experiment of Figure 1. Under no magnetic field, the superparamagnetic nanoparticles are well dispersed to form a homogeneous solution. Under magnetic field, the nanoparticles agglomerate at the bottom of the cuvette. It takes several hours to form the apparent agglomerate. As the particles agglomerate, the solution turns pale. The agglomerate does not change apparently thereafter even though the magnetic weight of the sample increases steadily, which indicates that the structural relaxation of the agglomerate undergoes continuously. When the magnetic field is removed without disturbance, the agglomerate remains as it is for a while but the nanoparticles of the agglomerate disperse and the original homogeneous solution is recovered in a short time.

3.2. Temporal change of magnetic weight
Figure 3 shows a temporal change of the magnetic weight of the sample at 30 T m$^{-1}$. The magnetic weight is set to zero when no magnetic field is applied. The magnetic weight of the sample jumps at the
instant of placing the sample on the balance. This jump is due to the Neel and Brown mechanisms[7] whose response times are much shorter than that of the electronic balance, a few msec. The slow growth of the magnetic weight after the jump $W(t)$ fits well to the stretched exponential function as following

$$W(t) = W(\infty) + [W(0) − W(\infty)] \exp[-(t/\tau)^\beta]$$

(2)

where $W(\infty)$ is the equilibrium magnetic weight and $W(0)$ corresponds to the magnetic weight by the Neel and Brown mechanisms. The exponential function with $0 < \beta < 1$ is called a stretched exponential. The fitting curve given as the red line in Figure 3 has the parameters of $W(0) = 1.090$ g, $W(\infty) = 2.454$ g, $\tau = 802$ min and $\beta = 0.802$. The magnetization calculated from the $W(\infty)$ is $1.38 \times 10^5$ A m$^{-1}$ which corresponds to 29% of the bulk magnetization of magnetite, $4.7 \times 10^5$ A m$^{-1}$. Deviation of the fitting curve from the measured magnetic weight results mainly from the temperature fluctuation, which is observed clearly when the laboratory temperature changes very much. The temperature effect on the magnetic weight is discussed below.

The stretched exponential behavior of the dynamics is observed when the energy barrier involved in the dynamics is not a single value but has some distribution, which is a characteristics of complicated processes.[8-10] The spectrum of energy barrier is wider for smaller $\beta$. With a proper expression of the rate constant such as the Arrhenius relation, the energy barrier distribution function can be determined by the inverse Laplace transform of the temporal behavior of the dynamics.[8,11] The data of Figure 3 gives the negatively skewed function for the energy barrier with the energy maximum of 52.3 kJ mol$^{-1}$ and the full width at the half maximum of 1.6 kJ mol$^{-1}$. Details of the process of determining the energy barrier distribution function is discussed in ref. 11.

Figure 2. Agglomeration of nanoparticles under magnetic field. It takes several hours for the nanoparticles to agglomerate at the bottom of a cuvette.

Figure 3. Temporal change of magnetic weight with the fitting curve of a stretched exponential function (red line). Two data overlap so well that it is not easy to see the difference.
Thermal motions of the nanoparticles of the agglomerate perturb the structural order of the agglomerate, which results in the decrease of magnetic weight. Figure 4 shows the magnetic weight of the sample measured in the cold winter season when the heating of the laboratory building is off and the laboratory temperature goes down at night time. Change of the magnetic weight by temperature fluctuation can be seen as a result of interconversion between the superparamagnetic-like state and the ferromagnetic-like state of the agglomerate. The fitting parameters of the data of Figure 4 are \( W(0) = 1.520 \, \text{g}, \ W(\infty) = 1.823 \, \text{g}, \ \tau = 560 \, \text{min} \) and \( \beta = 0.963 \). The magnetization estimated with the \( W(\infty) \) is \( 1.03 \times 10^5 \, \text{A m}^{-1} \) corresponding to 22% of the bulk magnetite magnetization. The magnetic weight increases faster and \( W(\infty) \) is smaller but \( W(0) \) is larger in Figure 4 compared with the data of Figure 3. The larger \( \beta \) of Figure 4 indicates that the energy barrier distribution is narrower in Figure 4.

The fitting curve of Figure 4 is considered as the magnetic weight at the average temperature. The magnetic weight greater than the fitting curve corresponds to the agglomerate whose temperature is lower than the average. As the heating of the laboratory building is on in the morning and the laboratory temperature begins to rise, the magnetic weight as well as the magnetization of the agglomerate decreases to be smaller than those at the average temperature. The enhanced thermal motions of nanoparticles may interrupt and block complicated pathways to the formation of the ordered agglomerate to retard the growth of the magnetic weight.

Figure 5 show the difference of the fitting curve and the measured magnetic weight \( \Delta W = W_{\text{fit}} - W_{\text{meas}} \) and the laboratory temperature. The laboratory temperature and the magnetic weight difference change synchronously, which suggests that the magnetic weight of the agglomerate can work as a thermometer. The temperature and the weight difference deviate somewhat at the beginning of agglomeration where the magnetite nanoparticles are dispersed in the whole solution and do not agglomerate at the bottom of the cuvette yet. Diffusion of nanoparticles along the magnetic field gradient is dominant at the early stage of agglomeration. After the agglomerate forms at the bottom and the magnetic weight reaches the almost flat slow increasing stage, the structural relaxation inside the agglomerate is a main cause for the magnetic weight growth. At this stage, the magnetic weight of the agglomerate becomes more sensitive to the temperature, that is, more synchronous with the temperature than at the early stage of agglomeration. As the agglomerate becomes mature, the deviation of the temperature and the magnetic weight reappear at shown in Figure 5. This deviation is different in the direction from that of the beginning of the dynamics, which suggests that the origins of the deviations are different. The agglomerate is not formed yet at the beginning of the dynamics while the internal structure of the agglomerate changes progressively after the formation.
3.4. Analysis of the magnetic weight fluctuation with Boltzmann distribution

In order to analyse the magnetic weight fluctuation with the Boltzmann distribution, it is assumed that the magnetic weight results from only the ferromagnetic-like state of the agglomerate and that thermal motions of the nanoparticles cause the transition to the superparamagnetic-like state which reduces the magnetic weight. The magnetic weight is assumed to be proportional to the relative ratio of the ferromagnetic-like state.

Eq. (3) shows the Boltzmann relation of the magnetic weight.\[12\] The nanoparticles of the agglomerate are assumed to be in the two-level system. The \( W_o \) corresponds to the magnetic weight when all the nanoparticles of the agglomerate are assumed to be at the ferromagnetic-like state. The \( W_o \) is the magnetic weight of the agglomerate at 0K, and the \( W_{\text{meas}} \) would approach one half of \( W_o \) when the temperature goes up. The \( W_{\text{meas}} \) is the magnetic weight of the agglomerate when the nanoparticles are distributed between the two states. Eqs. (4) and (5) are modifications of Eq. (3). As mentioned, the \( W_{\text{fit}} \) is the magnetic weight when the agglomerate is assumed to be at the average temperature, \( T_a \).

\[
\frac{W_o - W_{\text{meas}}}{W_{\text{meas}}} = \exp\left(-\frac{E_b}{RT}\right) \tag{3}
\]

\[
W_{\text{meas}} = W_o \left[1 + \exp\left(-\frac{E_b}{RT}\right)\right]^{-1} \tag{4}
\]

\[
W_{\text{fit}} = W_o \left[1 + \exp\left(-\frac{E_b}{RT_a}\right)\right]^{-1} \tag{5}
\]

where the \( E_b \) represents the energy difference between the two states. This energy difference is interpreted as the interparticle interaction energy in the agglomerate.

We have three measured parameters involved in the picture of the Boltzmann distribution, \( W_{\text{meas}} \), \( T \) and \( T_a \), and the \( W_{\text{fit}} \) from the fitting with the stretched exponential. From the ratio of \( W_{\text{meas}} \) and \( W_{\text{fit}} \), we can simulate the magnetic weight difference, \( W_{\text{meas}} - W_{\text{fit}} \) by varying \( E_b \). Figure 6 shows the measured and the simulated magnetic weight difference. The best fitting \( E_b \) is 4.1 \pm 0.1 \text{ kJ mol}^{-1}, which is similar as the weak hydrogen bond energy. This energy difference is smaller than the previously reported value of 7.6 \text{ kJ mol}^{-1}.\[12\] The variation of \( E_b \) reveals the complexity of the agglomerate. Both \( E_b \)’s are much smaller than the maximum of the energy barrier involved in the formation of the agglomerate.

In order to improve the agreement of the measured and the simulated magnetic weight at the beginning and the end of Figure 6, the \( E_b \) should change in opposite directions. The \( E_b \) should be raised at the beginning of the dynamics while it should be lowered at the end, which confirms that the characters of the dynamics are changing as the agglomeration goes on. At the beginning of the dynamics, the

![Figure 6. Difference of the measured magnetic weight and the fitting curve of Figure 4 (blue line) and the magnetic weight difference simulated with energy difference \( E_b \) of Eqs. (3)-(5) (red line).](image)
diffusion is dominant and loosely bonded agglomerate is formed. As the structural relaxation of the agglomerate goes on, the stable structure of the agglomerate is developing eventually.

4. Concluding Remarks

It is not easy to carry out accurately the measurement of magnetic weight in this work. Manual placement of the sample on the balance causes the variation of the magnetic field strength. Slow microscopic transformation and inhomogeneity of the nanoparticles in the solution sample could prevent the reproducibility of the experiments. However, the main obstacle of this work lies in the complexity of the agglomeration of nanoparticles itself. The agglomeration is not a single step process and there are so many different agglomerates with the same macroscopic properties and so many pathways to reach a specific agglomerate. Therefore, the energy landscape of the agglomeration[13] should be employed to understand the details of agglomeration. There are many big energy barriers for the formation of the agglomerate and small barriers for the stabilization of the agglomerate.

Nonetheless the two-level system works well for the explanation of thermal fluctuation of the magnetic weight. Instantaneous variation of the magnetic weight following the temperature change makes the magnetic weight act as a thermometer. Small interparticle interaction energy inside the agglomerate is important for the magnetic thermometer working at room temperature.

5. References

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