ELECTRONIC SUPPLEMENTARY INFORMATION

FERROGELS BASED ON ENTRAPPED METALLIC IRON NANOPARTICLES IN POLYACRYLAMIDE NETWORK: EXTENDED DERJAGUIN-LANDAU-VERWEY-OVERBEEK CONSIDERATION, INTERFACIAL INTERACTIONS AND MAGNETODEFORMATION

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Evaluation of Hamaker constant in Fe-water dispersion

We employed the method recently described by Pinchuk et. al.[1,2]. According to Lifshitz theory, the Hamaker constant can be written as

$$A_H = \frac{3}{4\pi}\hbar\omega_{Fe-H_2O-Fe} \quad \text{(S1)}$$

where, ω_{Fe-H_2O-Fe} is Lifshitz constant which can be approximated as

$$\omega_{Fe-H_2O-Fe} \approx \int_0^\infty \left(1 - \frac{2\varepsilon_{H_2O}(i\omega)}{\varepsilon_{H_2O}(i\omega) + \varepsilon_{Fe}(i\omega)}\right)^2 d\omega \quad \text{(S2)}$$

$\varepsilon_{H_2O}(i\omega)$ and $\varepsilon_{Fe}(i\omega)$ represent the dielectric permittivity of water and iron as a function of imaginary frequency (iω), respectively. Such permittivity of any medium can be written as

$$\varepsilon_n(i\omega) = 1 + \frac{2}{\pi}\int_0^\infty \frac{x\,\mathrm{Im}\,\varepsilon_n(x)}{x^2+\omega^2}\,dx \tag{S3}$$

The Lifshitz theory applied here using Equation S1 and S2 includes a first few important terms for the calculation of nonretarderd Hamaker constants. Theoretically, Equations (S2) and (S3) are calculated in entire frequency range, i.e. $0 < \omega < \infty$. But, experimental data for iron and water are only available in specific range, which is even narrower for water[3–6]. We used recently measured values of dielectric permittivity of water by Hayashi et. al.[4] There are two reasons for this choice. First, it covers a wider range i.e. 1-100 eV as compared to previously reported data for water by Hale et. al.[3] i.e. 0.006 – 6 eV, which were used for size dependent Hamaker constant calculations in previous reports.[1,2,7] Second, the measured data for optical constant and subsequently dielectric permittivity values in 1 - 7.2 eV range differ significantly in these two literatures.[3,4] A significant discrepancy in measured values of optical constants in high wavelength region for water is widely reported due to limited accuracy in experimental setup.[3,8,9] Due to these reasons, we opted for more reliable reported values[4] of dielectric permittivity in wider frequency range for water in calculations. Thus, lower and upper bounds for the integrals were set as 1 and 100 eV, respectively.

The size induced effect on ε_{Fe} was calculated using modified Drude model.[2] The Drude model is given as

$$\varepsilon_{Drude} = 1 - \frac{{\omega_p}^2}{\omega^2 + i\gamma_{bulk}\omega} \tag{S4}$$

where, $\omega_p = \sqrt{\frac{ne^2}{\varepsilon_o m}}$ and $\gamma_{bulk} = 0.01\omega_p$.

ω_p and γ_{bulk} are plasma frequency and electron damping constant for bulk iron, respectively. n = 17 X 10^{28} m^{-3}, e = 1.6 X 10^{-19} C, ε_o = 8.85 X 10^{-12} $F.m^{-1}$ and m = 9.1 X 10^{-31} kg are free electron density, electronic charge, vaccum permittivity and effective electron mass, respectively.[10] Finite size effect results in the change electron scattering rate which can be taken into account by writing it as

$$\gamma(D) = \gamma_{bulk} + 2A\frac{\upsilon_{Fe}}{D} \quad \text{(S5)}$$

where, ν_{Fe} = 1.98 X 10^6 $m.s^{-1}$ is the Fermi velocity of electron in iron[10], D is the diameter of nanoparticle, and coefficient A ≈ 1. Thus, modified Drude model incorporated with size effect can be written as

$$\varepsilon_{Drude}(D) = 1 - \frac{{\omega_p}^2}{\omega^2 + i\gamma(D)\omega} \quad \text{(S6)}$$

The modified permittivity values for nanosized iron ($\varepsilon_{\text{Fe nano}}(D)$) can be calculated using Equations (S4),(S5) and (S6), and bulk permittivity values of iron ($\varepsilon_{\text{Fe bulk}}(D)$) by[1,2]

$$\varepsilon_{\text{Fe nano}}(D) = \varepsilon_{\text{Fe bulk}} + \varepsilon_{Drude}(D) - \varepsilon_{Drude} \quad \text{(S7)}$$

Using above calculated values for iron and data for water from literature[4], the values were incorporated in Equations (S1) and (S2) for variable size of iron nanoparticles. The calculated values for Hamaker constants are shown in Figure S1. The values can be well represented by a third order exponential decay which was further used in xDLVO calculations.

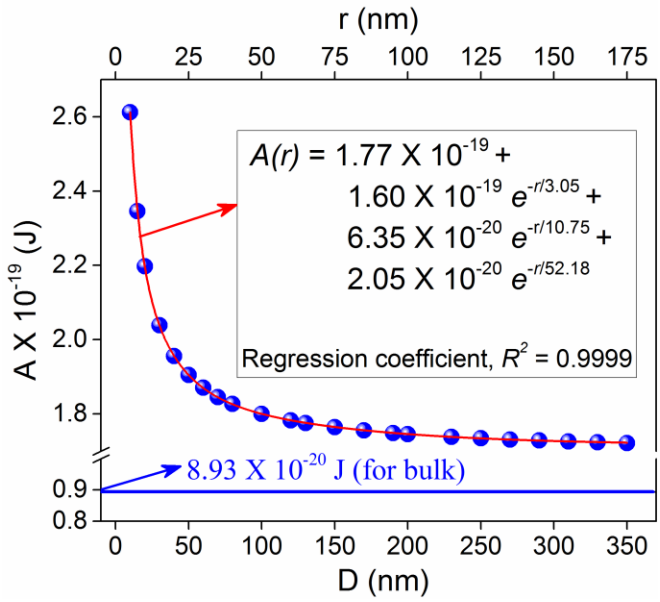

Figure S1. Size-dependent Hamaker constant for iron-water-iron system. Blue symbol and red line represents calculated points and exponential fit, respectively. Blue line represents Hamaker constant value for bulk iron.

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