Supplementary file

Small angle neutron scattering studies of shale oil occurrence status at nanopores

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Structural scale of closely-packed particles

In polydisperse systems, Guinier's approximation allows for structural analyses of widely-spaced particles by ignoring interparticle interactions (Guinier, 1939). The scattering intensity thereby follows an exponential decay with a slope of $-\frac{1}{3}(qR_g)^2$ at low q values where $qR_g < 1$ (Hammouda, 2012). When considering interparticle interactions, for polydisperse closely-packed particle system, the scattering intensity formula for ensembled particles is expressed as (Guinier et al., 1955):

$$I(q) = \sum_k p_k \overline{F_k^2(q)} + \sum_k \sum_j p_k p_j \overline{F_k(q)}\,\overline{F_j(q)} \frac{1}{v_a} \int_0^\infty \left[P_{kj}(r) - 1\right] \frac{\sin qr}{qr} 4\pi r^2 \mathrm{d}r \tag{S1}$$

Eq. (S1) is derived by considering the average orientations and positions of particles within the system. Here, p indicates the probability for one kind of particle, while $p_k = v_k/v_s$, v_a represents the average volume of all particles with:

$$v_k = N_k \frac{4\pi {r_k}^3}{3} \tag{S2}$$

$$v_s = \frac{v_p}{\phi_0} \tag{S3}$$

For Eq. (S1), v_a is expressed as:

$$v_a = \frac{v_p}{\sum_{k=1}^{n} N_k} \tag{S4}$$

and

$$v_p = \sum_{k=1}^{n} N_k \frac{4\pi {r_k}^3}{3} \tag{S5}$$

where v_k, v_s, v_a, and v_p denote the volume for k type of particle, total scattered sample volume, the average particle volume, and the total particle volume, respectively. Meanwhile, ϕ_0 is the sample porosity, and N is the number for each type of particle.

Within the first summation of Eq. (S1), $F_k(q)$ denotes the form factor, which is the Fourier transform of the scattering length $\rho_k(r)$ for particle of type k, as shown in Eq. (S7). The first summation term reflects the mean squared form factor of size and shape information for a collection of type k particles, as shown in Eq. (S8). For particles with spherical symmetry, this simplifies to $\overline{F^2(q)} = \overline{F(q)^2} = F^2(q)$.

$$F_k(q) = \int \rho_k(r)\mathrm{e}^{iq\cdot r}\mathrm{d}x \tag{S6}$$

$$\overline{F^2(q)} = \sum\nolimits_k p_k \overline{F_k^2(q)} \tag{S7}$$

For the consideration of the particle interactions in the second sum term, the radial distribution function for a pair of spherical particles (Yuste and Santos , 1991), $P_{kj}(r)$, describes how particle density varies as a function of distance r from a reference particle, which is connected to the probability of seeing a certain configuration of two particles realized. $P_{kj}(r)$ essentially jumps from 0 to 1 at the diameter of the hard spheres because particles cannot overlap but do not interact otherwise, which expressed as a step function (A9):

$$P_{kj}(r) = \begin{cases} 0 & \text{if } 0 < r < 2R \\ 1 & \text{if } r > 2R \end{cases} \tag{S8}$$

where R is the radius of the spheres.

For closely-packed systems, when neglecting complex interactions and only consider the interactions of particles as both individuals and pairs, the probability of finding the particles separated by a distance r is given by $e^{-\mathrm{v}(r)/kT}$, as described by Raman (1924). Built upon the Kirkwood-Boggs principle of superposition (Kirkwood and Boggs, 1942), for particle interactions beyond simple units and in pairs which extending to a system with multiple pairs governed by central forces over a distance r, Rodriguez applied the theory of Born and Green (cf. Fournet, 1951) to define the pair distribution function $P_{kj}(r)$ as follows (Yuste and Santos, 1991):

$$P_{kj}(r) = \mathrm{e}^{-\frac{\mathrm{v}_{kj}(r)}{kT}+f_{kj}(r)} \tag{S9}$$

In Eq. (S10), the pairwise potential, $v_{kj}(r)$, characterizes the interaction energy between two particles of types k and j separated by a distance r, while k and T are the Boltzmann constant and temperature. The function $P_{kj}(r)$ gives the probability of finding a particle of type j at a distance r from a particle of type k, while the function $f_{kj}(r)$ modifies the radial distribution function to account for additional correlations beyond simple pairwise interactions, which describe the effects of the surrounding medium on the pair distribution.

Additionally, two functions are introduced here, $g_{kj}(q)$ and $\beta_{kj}(q)$, which relate to Eq. (S11) and Eq. (S12) through their Fourier transforms, respectively. These functions are ultimately interconnected through a set of relationships through Eq. (S13).

$$g_{kj}(q) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} r^2 f_{kj}(r)\frac{\sin qr}{qr}\,\mathrm{d}r \tag{S10}$$

$$\beta_{kj}(q) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} r^2\left(e^{-\frac{\mathrm{v}_{kj}(r)}{kT}} - 1\right)\frac{\sin qr}{qr}\,\mathrm{d}r \tag{S11}$$

$$\frac{v_0}{(2\pi)^{\frac{3}{2}}}g_{kj}(q) = \sum_i p_i[g_{ki}(q) + \epsilon_{ki}\beta_{ki}(q)]\epsilon_{ij}\beta_{ij}(q) \tag{S12}$$

Specifically, $\beta_{kj}(q)$ is the Fourier transform of the pairwise potential $\mathrm{v}_{kj}(r)$ which contribution to the $F_k(q)$. Eq. (S8) implies that a mixture of form factor can be constructed from the form factors of the individual components represented by $g_{ki}(q)$ and $\beta_{ki}(q)$, along with their interactions represented by $\epsilon_{ij}\beta_{ij}(q)$. The ϵ_{jk} designates a mean value of $f_{jk}(r) + 1$ near the origin, $r = 0$, which would influence the short-range order in the system. For an in-depth explanation of these connections, readers are directed to (Guinier et al., 1955). By the virtue of these introduced functions, substitute the $P_{kj}(r)$ through $g_{kj}(q)$ and $g_{kj}(q)$ functions, Eq. (S1) becomes:

$$I(q) = \sum_{k} p_k \overline{F_k^2(q)} + \frac{(2\pi)^{3/2}}{v_a} \sum_{k} \sum_{j} p_k p_j \overline{F_k(q)}\,\overline{F_j(q)}\left[g_{kj}(q) + \epsilon_{kj} \beta_{kj}(q)\right] \tag{S13}$$

Notably, $\overline{F^2(q)}$ is the average intensity distributions for particles of different shapes which take all orientations with equal probability, for spherical system with the radius r, the form factor can be expressed as (Rayleigh, 1914):

$$\overline{F_k^2(q)} = \rho_k^2(r) {v_k}^2 \Phi^2(qr) = \phi_k v_k \rho_k^2(r) \Phi^2(qr_k) \tag{S14}$$

Here, $\Phi(qr)$ is expressed in two different ways that either using sine and cosine functions or using the spherical Bessel function of the first kind $J_{3/2}(hR)$.

$$\Phi^2(qr) = \left[3\frac{\sin(qr) - qr\cos(qr)}{(qr)^3}\right]^2 = \frac{9\pi}{2}\left[\frac{J_{\frac{3}{2}}(qr)}{(qr)^{\frac{3}{2}}}\right]^2 \tag{S15}$$

Taking $qr = \alpha$, Eq. (S16) is expressed as

$$\Phi(\alpha) = 3\frac{\sin\alpha - u\cos\ \alpha}{(\alpha)^3} \tag{S16}$$

Since Eq. (S14) begins with gas-like systems as a starting point. Considering hard spheres where the potential $v_{kj}(r)$ becomes infinite for $r < 2R$, for the purposes of this analysis, ϵ_{kj} is assumed to equal 1, and $g_{kj}(q)$ is set to 0.

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