SUPPLEMENTARY DOCUMENT

Integrating Process

Choosing $F(\gamma)$ as a general representation of the functions including a parameter , which refers to the separation angel between the two rods

$$\zeta = \iint F(\gamma) f(\Omega_1) f(\Omega_2) d\Omega_1 d\Omega_2 \tag{1}$$

$$d\Omega = \sin\theta d\theta d\phi \tag{2}$$

The Onsager trial function is used as the orientational function

$$\begin{aligned}\zeta &= \iint\iint F(\gamma) \frac{\alpha_1 \cosh(\alpha_1 \cos\theta_1)}{4\pi \sinh(\alpha_1)} \frac{\alpha_2 \cosh(\alpha_2 \cos\theta_2)}{4\pi \sinh(\alpha_2)} \sin\theta_1 d\theta_1 d\phi_1 \sin\theta_2 d\theta_2 d\phi \\ &= K \iint\iint F(\gamma) \cosh(\alpha_1 \cos\theta_1) \cosh(\alpha_2 \cos\theta_2) \sin\theta_1 d\theta_1 d\phi_1 \sin\theta_2 d\theta_2 d\phi_2\end{aligned} \tag{3}$$

$$K = \frac{\alpha_1 \alpha_2}{16\pi^2 \sinh(\alpha_1) \sinh(\alpha_2)} \tag{4}$$

According to the product to sum formula of hyperbolic functions

$$\begin{aligned}\zeta = \frac{K}{2} \{ &\int_{\phi_1} \int_{\phi_2} \int_{\theta_1} \int_{\theta_2} \cosh(\alpha_1 \cos\theta_1 + \alpha_2 \cos\theta_2) \sin\theta_1 \sin\theta_2 d\theta_1 d\phi_1 d\theta_2 d\phi_2 \\ &+ \int_{\phi_1} \int_{\phi_2} \int_{\theta_1} \int_{\theta_2} \cosh(\alpha_1 \cos\theta_1 - \alpha_2 \cos\theta_2) \sin\theta_1 \sin\theta_2 d\theta_1 d\phi_1 d\theta_2 d\phi_2 \}\end{aligned} \tag{5}$$

For the first time, a variable substitution skill is used, $\tau = \pi - \theta_2$, then

$$\begin{aligned}\zeta = \frac{K}{2} \{ &\int_{\phi_1} \int_{\phi_2} \int_{\theta_1} \int_{\theta_2=0}^{\pi} F(\gamma) \cosh(\alpha_1 \cos\theta_1 + \alpha_2 \cos\theta_2) \sin\theta_1 \sin\theta_2 d\theta_1 d\phi_1 d\theta_2 d\phi_2 \\ &- \int_{\phi_1} \int_{\phi_2} \int_{\theta_1} \int_{\tau=0}^{\pi} F(\gamma) \cosh(\alpha_1 \cos\theta_1 + \alpha_2 \cos\tau) \sin\theta_1 \sin\tau d\theta_1 d\phi_1 d\tau d\phi_2 \}\end{aligned} \tag{6}$$

The integrating process has no concern with the label of the variables, so the Eq(6) can be simplified to

$$\zeta = 2K\pi \int_{\phi} \int_{\theta_1} \int_{\gamma} F(\gamma) \cosh(\alpha_1 \cos\theta_1 + \alpha_2 \cos\theta_2) \sin\theta_1 \sin\gamma d\theta_1 d\gamma d\phi \tag{7}$$

$$\zeta = K\int_{\phi_1}\int_{\phi_2}\int_{\theta_1}\int_{\theta_2} F(\gamma)\cosh(\alpha_1\cos\theta_1 + \alpha_2\cos\theta_2)\sin\theta_1\sin\theta_2 d\theta_1 d\phi_1 d\theta_2 d\phi_2 \tag{8}$$

The coordinate is rotated as depicted in the addendum of Onsager's original work , so that γ and θ_1 are chose for convenience instead of θ_1 and θ_2. One azimuthal angle can be integrated out, and the remaining one is used a new variable $\phi = \phi_1 - \phi_2$, then the expression becomes

$$\zeta = 2K\pi\int_{\phi}\int_{\gamma}\int_{\theta_1} F(\gamma)\cosh(\alpha_1\cos\theta_1 + \alpha_2\cos\theta_2)\sin\theta_1\sin\gamma d\theta_1 d\phi d\gamma \tag{9}$$

For the third time the variable substitution is applied

$$\cos\theta_1 = \sin\chi\cos(\psi + f(\gamma)) \tag{10}$$

$$\sin\theta_1\cos\phi = \sin\chi\sin(\psi + f(\gamma)) \tag{11}$$

$$\tan f(\gamma) = \frac{\alpha_2\sin\gamma}{\alpha_1 + \alpha_2\sin\gamma} \tag{12}$$

The Jacobian used in the substituting the integration variables is

$$\frac{\partial(\theta_1,\phi)}{\partial(\chi,\psi)} = \frac{\sin\chi}{\sin\psi} \tag{13}$$

Then

$$\begin{aligned}\zeta = 2K\pi\int_{\phi=0}^{\pi}\int_{\chi=0}^{\pi}\int_{\psi=0}^{2\pi} & F(\gamma)\sin\chi\sin\gamma d\chi d\psi d\gamma \\ & \cosh\left[\left(\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2\cos\gamma\right)^{1/2}\sin\chi\cos\psi\right]\end{aligned} \tag{14}$$

The final transformation of the integral is based on

$$\sin\chi\cos\psi = \cos\mu \tag{15}$$

$$\cos\chi = \sin\mu\cos\xi \tag{16}$$

The Jacobian is

$$\frac{\partial(\chi,\psi)}{\partial(\mu,\xi)}=\frac{\sin\mu}{\sin\chi} \tag{17}$$

After simplification

$$\begin{aligned}\zeta = 2K\pi\int_{\phi=0}^{\pi}\int_{\mu=0}^{\pi}\int_{\xi=0}^{2\pi} F(\gamma)\sin\mu\sin\gamma\, d\mu\, d\xi\, d\gamma \\ \cosh\left[\left(\alpha_1^{\ 2}+\alpha_2^{\ 2}+2\alpha_1\alpha_2\cos\gamma\right)^{1/2}\cos\mu\right]\end{aligned} \tag{18}$$

The variable ξ can be directly integrated out and

$$\begin{aligned}\zeta &= 4K\pi^2\int_{\gamma=0}^{\pi}\int_{\mu=0}^{\pi} F(\gamma)\cosh\left[\left(\alpha_1^{\ 2}+\alpha_2^{\ 2}+2\alpha_1\alpha_2\cos\gamma\right)^{1/2}\cos\mu\right]\sin\gamma\, d\gamma\, d\cos\mu \\ &= 4K\pi^2\int_{\gamma=0}^{\pi} F(\gamma)\sin\gamma\left\{\frac{2\sinh\left[\left(\alpha_1^{\ 2}+\alpha_2^{\ 2}+2\alpha_1\alpha_2\cos\gamma\right)^{1/2}\right]}{\left(\alpha_1^{\ 2}+\alpha_2^{\ 2}+2\alpha_1\alpha_2\cos\gamma\right)^{1/2}}\right\}d\gamma\end{aligned} \tag{19}$$

Apparently when $\cos\gamma$ is seen as the variable

$$\begin{aligned}\zeta &= 4K\pi^2\int_{\gamma=0}^{\pi} F(\gamma)\left\{\frac{2\sinh\left[\left(\alpha_1^{\ 2}+\alpha_2^{\ 2}+2\alpha_1\alpha_2\cos\gamma\right)^{1/2}\right]}{\left(\alpha_1^{\ 2}+\alpha_2^{\ 2}+2\alpha_1\alpha_2\cos\gamma\right)^{1/2}}\right\}d\cos\gamma \\ &= \frac{-8K\pi^2}{\alpha_1\alpha_2}\int_{\gamma=0}^{\pi} F(\gamma)\, d\cosh\left[\left(\alpha_1^{\ 2}+\alpha_2^{\ 2}+2\alpha_1\alpha_2\cos\gamma\right)^{1/2}\right]\end{aligned} \tag{20}$$

Integrated by parts

$$\begin{aligned}\zeta = \frac{-8K\pi^2}{\alpha_1\alpha_2}F(\gamma)\cosh\left[\left(\alpha_1^{\ 2}+\alpha_2^{\ 2}+2\alpha_1\alpha_2\cos\gamma\right)^{1/2}\right]_{\gamma=0}^{\pi} \\ +\frac{8K\pi^2}{\alpha_1\alpha_2}\int_{\gamma=0}^{\pi}\cosh\left[\left(\alpha_1^{\ 2}+\alpha_2^{\ 2}+2\alpha_1\alpha_2\cos\gamma\right)^{1/2}\right]dF(\gamma)\end{aligned} \tag{21}$$

The rod model has a symmetry requirement, that

$$F(\gamma)=F(\pi-\gamma) \tag{22}$$

Therefore,

$$\zeta = \frac{-8K\pi^2}{\alpha_1\alpha_2}F(0)\left[\cosh(\alpha_1+\alpha_2)-\cosh(\alpha_1-\alpha_2)\right]$$

$$+\frac{8K\pi^2}{\alpha_1\alpha_2}\int_{\gamma=0}^{\pi}\cosh\left[\left(\alpha_1^2+\alpha_2^2+2\alpha_1\alpha_2\cos\gamma\right)^{1/2}\right]dF(\gamma) \tag{23}$$

$$=\frac{1}{2\sinh\alpha_1\sinh\alpha_2}\int_{\gamma=0}^{\pi}\cosh\left[\left(\alpha_1^2+\alpha_2^2+2\alpha_1\alpha_2\cos\gamma\right)^{1/2}\right]dF(\gamma)+F(0)$$

And when the rods are in the same shape $\alpha=\alpha_1=\alpha_2$,

$$\zeta=\frac{1}{2\sinh^2\alpha}\int_{\gamma=0}^{\pi}\cosh\left[\alpha\left(2+2\cos\gamma\right)^{1/2}\right]dF(\gamma)+F(0) \tag{24}$$

Or

$$\zeta=\frac{1}{2\sinh^2\alpha}\int_{\gamma=0}^{\pi}\cosh\left[2\alpha\cos\left(\frac{\gamma}{2}\right)\right]dF(\gamma)+F(0) \tag{25}$$

The $F(\gamma)$ used in the article is base on the excluded volume and the integration used in both thesteric part and perturbative part involves a expression as

$$F(\gamma)=\sum_i C_i\left|\sin^i\gamma\right| \tag{26}$$

When the index is even, the Eq 24 is used

$$\begin{aligned}\zeta_{2n} &= \iint \sin^{2n}\gamma f(\Omega_1)f(\Omega_2)d\Omega_1 d\Omega_2\\ &=\frac{n}{\sinh^2\alpha}\int_0^{\pi}\cosh\left(\alpha\left[2(1+\cos\gamma)\right]^{1/2}\right)\sin^{2n-1}\gamma\cos\gamma d\gamma\end{aligned} \tag{27}$$

A simple variable substitution is applied

$$\mu=(1+\cos\gamma)^{1/2} \tag{28}$$

Then

$$
\begin{aligned}
\zeta_{2n} &= \iint \sin^{2n}\gamma f\left(\Omega_1\right) f\left(\Omega_2\right) d\Omega_1 d\Omega_2 \\
&= \frac{n}{\sinh^2\alpha}\int_0^{2^{1/2}} \cosh\left(\alpha 2^{1/2}\mu\right)\left(\mu^2-1\right)\mu\left(2\mu^2-\mu^4\right)^{n-1} d\mu \\
&= \frac{n}{\sinh^2\alpha}\sum_j C_j^{'}\int_0^{2^{1/2}} \cosh\left(\alpha 2^{1/2}\mu\right)\mu^j d\mu
\end{aligned} \tag{29}
$$

Where $C_j^{'}$ is a constant which depends on the index and calculated by part integral. On the other hand, when the index is odd, the Eq(25) is used

$$
\begin{aligned}
\zeta_{2n+1} &= \iint \left|\sin^{2n+1}\gamma\right| f\left(\Omega_1\right) f\left(\Omega_2\right) d\Omega_1 d\Omega_2 \\
&= \frac{2n+1}{2\sinh^2\alpha}\int_0^{\pi} \cosh\left(2\alpha\cos\left(\frac{\gamma}{2}\right)\right)\sin^{2n}\gamma\cos\gamma d\gamma \\
&= \frac{2n+1}{2\sinh^2\alpha}\int_0^{\pi} \cosh\left(2\alpha\cos\left(\frac{\gamma}{2}\right)\right)\left(1-\cos^2\gamma\right)^n\cos\gamma d\gamma \\
&= \frac{2n+1}{2\sinh^2\alpha}\sum_{i=0}^{n} C_i\int_0^{\pi} \cosh\left(2\alpha\cos\left(\frac{\gamma}{2}\right)\right)\cos^{2i+1}\gamma d\gamma
\end{aligned} \tag{30}
$$

Where C_i is the coefficient of the binomial. When the index of a cosine function is odd, then the expression can be written as a algebraic combination of cosine functions of multipule γ, therefore

$$
\zeta_{2n+1} = \frac{1}{2\sinh^2\alpha}\sum_j C_j^{"}\int_0^{\pi} \cosh\left(2\alpha\cos\left(\frac{\gamma}{2}\right)\right)\cos j\gamma d\gamma \tag{31}
$$

Where $C_j^{"}$ is a constant based on the coefficient of the binomial and the exact expression of the cosine functions

$$
\begin{aligned}
\zeta_j^{'} &= C_j^{'}\int_0^{\pi}\cosh\left(2\alpha\cos\left(\frac{\gamma}{2}\right)\right)\cos j\gamma d\gamma \\
&= 2C_j^{'}\int_0^{\frac{\pi}{2}}\cosh\left(2\alpha\cos\left(\mu\right)\right)\cos 2j\mu d\mu \\
&= C_j^{'}\left[\int_0^{\frac{\pi}{2}}\exp\left(2\alpha\cos\mu\right)\cos 2j\mu d\mu+\int_0^{\frac{\pi}{2}}\exp\left(-2\alpha\cos\mu\right)\cos 2j\mu d\mu\right] \\
&= C_j^{'}\left[\int_0^{\frac{\pi}{2}}\exp\left(2\alpha\cos\mu\right)\cos 2j\mu d\mu-\int_{\pi}^{\frac{\pi}{2}}\exp\left(2\alpha\cos\mu\right)\cos 2j\mu d\mu\right] \\
&= C_j^{'}\int_0^{\pi}\exp\left(2\alpha\cos\mu\right)\cos 2j\mu d\mu = C_j^{'}\pi I_{2j}\left(2\alpha\right)
\end{aligned}
\tag{32}
$$

Where $I_{2j}\left(2\alpha\right)$ is the modified Bessel function, therefore

$$
\begin{aligned}
\zeta_{2n+1} &= \iint\left|\sin^{2n+1}\gamma\right| f\left(\Omega_1\right) f\left(\Omega_2\right) d\Omega_1 d\Omega_2 \\
&= \frac{\pi\left(2n+1\right)}{2\sinh^2\alpha}\sum_j C_j^{'} I_{2j}\left(2\alpha\right)
\end{aligned}
\tag{33}
$$

These are as the general integral process and the three can be applied in the article take the form

$$
\begin{aligned}
\zeta_1 &= \iint\left|\sin\gamma\right| f\left(\Omega_1\right) f\left(\Omega_2\right) d\Omega_1 d\Omega_2 \\
&= \frac{\pi}{2\sinh^2\alpha} I_2\left(2\alpha\right)
\end{aligned}
\tag{34}
$$

$$
\begin{aligned}
\zeta_2 &= \iint\left|\sin^2\gamma\right| f\left(\Omega_1\right) f\left(\Omega_2\right) d\Omega_1 d\Omega_2 \\
&= \frac{1}{\sinh^2\alpha}\{\sinh\left(2\alpha\right)(\frac{2}{\alpha}+\frac{6}{\alpha^3}) \\
&\quad -\cosh\left(2\alpha\right)\left(\frac{5}{\alpha^2}+\frac{3}{\alpha^4}\right)-\frac{1}{\alpha^2}+\frac{3}{\alpha^4}\}
\end{aligned}
\tag{35}
$$

$$
\begin{aligned}
\zeta_3 &= \iint\left|\sin^3\gamma\right| f\left(\Omega_1\right) f\left(\Omega_2\right) d\Omega_1 d\Omega_2 \\
&= \frac{3\pi}{8\sinh^2\alpha}\left[I_2\left(2\alpha\right)-I_6\left(2\alpha\right)\right]
\end{aligned}
\tag{36}
$$

Results using the diameter d as one of the adjusted parameters

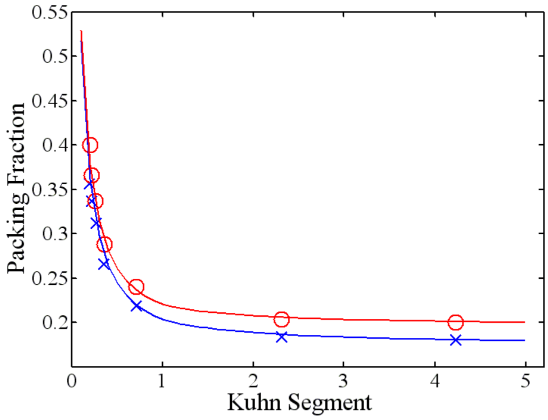

Fig. A1 The chain length dependence of η_i and η_a for PHIC in toluene at 25℃. Circles and squares are the experimental data of the two phases, respectively. The solid lines are the results given by Eq. (5) with the parameters of $d = 1.55\,\mathrm{nm}$, $\varepsilon_0 / kT = 1\times10^{-3}$, $\varepsilon_2 / kT = 3\times10^{-4}$.

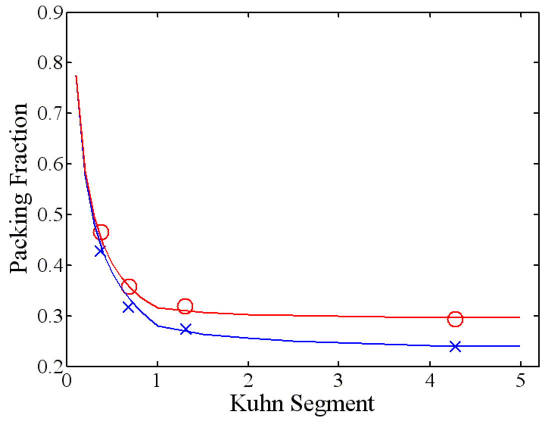

Fig. A2 The chain length dependence of η_i and η_a for PHIC in DCM at 20℃. Circles and squares are the experimental data of the two phases, respectively. The solid lines are the results given by Eq. (5) with the parameters of $d = 2\,\mathrm{nm}$, $\varepsilon_0 / kT = 2.2\times10^{-2}$, $\varepsilon_2 / kT = 8.5\times10^{-4}$.