

Supporting information for:

Phase Equilibria of Polydisperse Square-Well Chain Fluid Confined in Random Porous Media: TPT of Wertheim and Scaled Particle Theory

Taras V. Hvozď,[†] Yuriy V. Kalyuzhnyi,^{*,†} and Peter T. Cummings[‡]

[†]*Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine -
1 Svientsitskii St., Lviv, Ukraine 79011*

[‡]*Department of Chemical and Biochemical Engineering, Vanderbilt University, Nashville,
TN 37235-1604, USA*

E-mail: yukal@icmp.lviv.ua

1 SPT2b1 approximation

$$\frac{\beta A_{HS}^{SPT2b1}}{V} = \beta \sum_m \rho(m) \mu_{HS}^{SPT2b1}(m) - \beta P_{HS}^{SPT2b1}, \quad (S1)$$

$$\begin{aligned} \beta \mu_{HS}^{SPT2b1}(m) = m \left[\beta \mu_1^{(ex)} - \ln(1 - \eta/\phi_0) + (1 + a) \frac{\eta/\phi_0}{1 - \eta/\phi_0} \right. \\ \left. + \frac{\eta(\phi_0 - \phi)}{\phi_0 \phi (1 - \eta/\phi_0)} + \frac{(a + 2b)}{2} \frac{(\eta/\phi_0)^2}{(1 - \eta/\phi_0)^2} + \frac{2b}{3} \frac{(\eta/\phi_0)^3}{(1 - \eta/\phi_0)^3} \right], \end{aligned} \quad (S2)$$

$$\beta P_{HS}^{SPT2b1} = L_m \left[\frac{1}{1 - \eta/\phi_0} \frac{\phi_0}{\phi} + \left(\frac{\phi_0}{\phi} - 1 \right) \frac{\phi_0}{\eta} \ln \left(1 - \frac{\eta}{\phi_0} \right) + \frac{a}{2} \frac{\eta/\phi_0}{(1 - \eta/\phi_0)^2} + \frac{2b}{3} \frac{(\eta/\phi_0)^2}{(1 - \eta/\phi_0)^3} \right] - L_m, \quad (S3)$$

and $\phi = \exp(-\beta\mu_1^{(ex)})$, where the coefficients a and b define the porous media structure and for HS fluid in HS matrix

$$a = 6 + \frac{3\eta_0\tau(\tau + 4)}{1 - \eta_0} + \frac{9\eta_0^2\tau^2}{(1 - \eta_0)^2}, \quad (S4)$$

$$b = \frac{9}{2} \left(1 + \frac{\tau\eta_0}{1 - \eta_0} \right)^2, \quad \tau = \frac{\sigma}{\sigma_0}, \quad (S5)$$

$$\begin{aligned} \beta\mu_1^{(ex)} = & -\ln(1 - \eta_0) + \frac{9\eta_0^2}{2(1 - \eta_0)^2} - \eta_0 Z_0 + \eta_0 Z_0(1 + \tau)^3 \\ & + \left[3\eta_0 Z_0 - \frac{3\eta_0(1 + 2\eta_0)}{(1 - \eta_0)^2} \right] (1 + \tau) - \left[3\eta_0 Z_0 - \frac{3\eta_0(2 + \eta_0)}{2(1 - \eta_0)^2} \right] (1 + \tau)^2, \end{aligned} \quad (S6)$$

and

$$Z_0 = \frac{(1 + \eta_0 + \eta_0^2)}{(1 - \eta_0)^3}. \quad (S7)$$

2 Percus-Yevick radial distribution function of hard-sphere fluid in a matrix

Here we are using the hard-sphere radial distribution function obtained by Wertheim from Percus-Yevick approximation.¹ In the first shell $1 < r \leq 2$ we have

$$g_{HS}(r, \eta_{eff}[L_1]) = \frac{1}{3r} \frac{1}{(1 - \eta_{eff})^2} \sum_{l=0}^2 \sum_{k=0}^2 H_{kj}^{kl} \exp[t_l(r - 1)], \quad (S8)$$

where

$$H_0 = 1 + \frac{1}{2}\eta_{eff} , \quad (S9)$$

$$H_1 = -\frac{1}{4\eta_{eff}} \frac{1}{\sqrt{q^2 + \frac{1}{8}}} \left[x_-^2 (1 - 3\eta_{eff} - 4\eta_{eff}^2) + x_+ \left(1 - \frac{5}{2}\eta_{eff}^2 \right) \right] , \quad (S10)$$

$$H_2 = \frac{1}{4\eta_{eff}} \frac{1}{\sqrt{q^2 + \frac{1}{8}}} \left[x_+^2 (1 - 3\eta_{eff} - 4\eta_{eff}^2) + x_- \left(1 - \frac{5}{2}\eta_{eff}^2 \right) \right] , \quad (S11)$$

$$t_l = \frac{2\eta_{eff}}{1 - \eta_{eff}} \left[-1 + x_+ j^l + x_- j^{-l} \right] , \quad j = \exp \left(\frac{2}{3}\pi i \right) , \quad (S12)$$

$$x_{\pm} = \sqrt[3]{q \pm \sqrt{q^2 + \frac{1}{8}}} , \quad q = \frac{3 + 3\eta_{eff} - \eta_{eff}^2}{4\eta_{eff}^2} . \quad (S13)$$

3 Monomer contribution to thermodynamic properties

After integration, the expressions for Helmholtz free energy (14) and (15) are reduced to

$$\frac{\beta A_1}{V} = -2\pi L_1^2 \beta \epsilon G_{HS}(\eta_{eff}[L_1]) , \quad (S14)$$

$$\frac{\beta A_2}{V} = -\pi L_1^2 \beta^2 \epsilon^2 K^{HS} G_{HS}(\eta_{eff}[L_1]) , \quad (S15)$$

where

$$G_{HS}(\eta_{eff}[L_1]) = \frac{1}{3} \frac{1}{(1 - \eta_{eff})^2} \sum_{l=0}^2 \sum_{k=0}^2 H_{kj}^{kl} \Delta \tilde{S}_l(\eta_{eff}[L_1]) , \quad (S16)$$

$$\Delta \tilde{S}_l(\eta_{eff}[L_1]) = \tilde{S}_l(\lambda\sigma, \eta_{eff}[L_1]) - \tilde{S}_l(\sigma, \eta_{eff}[L_1]) , \quad (S17)$$

$$\tilde{S}_l(r, \eta_{eff}[L_1]) = \frac{e^{t_l(r-1)}}{t_l^2} (t_l r - 1) . \quad (S18)$$

Differentiating the expressions for Helmholtz free energy (S14) and (S15) with respect to the density we get the expressions for the chemical potentials

$$\beta\mu_1(m) = -2\pi\beta\epsilon mL_1 \left[2G_{HS}(\eta_{eff}[L_1]) + \eta \frac{\partial\eta_{eff}}{\partial\eta} \frac{\partial G_{HS}(\eta_{eff}[L_1])}{\partial\eta_{eff}} \right], \quad (S19)$$

$$\begin{aligned} \beta\mu_2(m) = & -\pi\beta^2\epsilon^2 mL_1 \left\{ G_{HS}(\eta_{eff}[L_1]) \eta \frac{\partial K^{HS}}{\partial\eta} \right. \\ & \left. + K^{HS} \left[2G_{HS}(\eta_{eff}[L_1]) + \eta \frac{\partial\eta_{eff}}{\partial\eta} \frac{\partial G_{HS}(\eta_{eff}[L_1])}{\partial\eta_{eff}} \right] \right\}, \end{aligned} \quad (S20)$$

where

$$\begin{aligned} \frac{\partial\eta_{eff}}{\partial\eta} = & -\frac{1}{g_{(HS)}^{(SPT)}(\sigma^+, \eta, \eta_0)} \left[\frac{1 - \sqrt{1 + 24g_{(HS)}^{(SPT)}(\sigma^+, \eta, \eta_0)}}{4g_{(HS)}^{(SPT)}(\sigma^+, \eta, \eta_0)} \right. \\ & \left. + \frac{3}{\sqrt{1 + 24g_{(HS)}^{(SPT)}(\sigma^+, \eta, \eta_0)}} \right] \frac{\partial g_{(HS)}^{(SPT)}(\sigma^+, \eta, \eta_0)}{\partial\eta}, \end{aligned} \quad (S21)$$

$$\frac{\partial g_{(HS)}^{(SPT)}(\sigma^+, \eta, \eta_0)}{\partial\eta} = \frac{5}{2} \frac{1}{(\phi_0 - \eta)^2} + \frac{3(\eta + \eta_0\tau)}{(\phi_0 - \eta)^3}, \quad (S22)$$

$$\begin{aligned} \frac{\partial G_{HS}(\eta_{eff}[L_1])}{\partial\eta_{eff}} = & \frac{1}{3(1 - \eta_{eff})^2} \left\{ 6(1 - \eta_{eff})G_{HS}(\eta_{eff}[L_1]) \right. \\ & \left. + \sum_{l=0}^2 \sum_{k=0}^2 j^{kl} \left[\frac{\partial H_k}{\partial\eta_{eff}} \Delta \tilde{S}_l(\eta_{eff}[L_1]) + H_k \frac{\partial \Delta \tilde{S}_l(\eta_{eff}[L_1])}{\partial\eta_{eff}} \right] \right\}, \end{aligned} \quad (S23)$$

$$\frac{\partial H_0}{\partial\eta_{eff}} = \frac{1}{2}, \quad (S24)$$

$$\begin{aligned} \frac{\partial H_1}{\partial \eta_{eff}} = & -\frac{H_1}{\eta_{eff}} - \frac{qH_1}{q^2 + \frac{1}{8}} \frac{\partial q}{\partial \eta_{eff}} - \frac{1}{4\eta_{eff}} \frac{1}{\sqrt{q^2 + \frac{1}{8}}} \left[2x_-(1 - 3\eta_{eff} \right. \\ & \left. - 4\eta_{eff}^2) \frac{\partial x_-}{\partial \eta_{eff}} - x_-^2 (3 + 8\eta_{eff}) + \left(1 - \frac{5}{2}\eta_{eff}^2 \right) \frac{\partial x_+}{\partial \eta_{eff}} - 5\eta_{eff}x_+ \right], \end{aligned} \quad (S25)$$

$$\begin{aligned} \frac{\partial H_2}{\partial \eta_{eff}} = & -\frac{H_2}{\eta_{eff}} - \frac{qH_2}{q^2 + \frac{1}{8}} \frac{\partial q}{\partial \eta_{eff}} + \frac{1}{4\eta_{eff}} \frac{1}{\sqrt{q^2 + \frac{1}{8}}} \left[2x_+(1 - 3\eta_{eff} \right. \\ & \left. - 4\eta_{eff}^2) \frac{\partial x_+}{\partial \eta_{eff}} - x_+^2 (3 + 8\eta_{eff}) + \left(1 - \frac{5}{2}\eta_{eff}^2 \right) \frac{\partial x_-}{\partial \eta_{eff}} - 5\eta_{eff}x_- \right], \end{aligned} \quad (S26)$$

$$\frac{\partial x_{\pm}}{\partial \eta_{eff}} = \frac{1}{3} \left(q \pm \sqrt{q^2 + \frac{1}{8}} \right)^{-\frac{2}{3}} \left[1 \pm \frac{q}{\sqrt{q^2 + \frac{1}{8}}} \right] \frac{\partial q}{\partial \eta_{eff}}, \quad (S27)$$

$$\frac{\partial q}{\partial \eta_{eff}} = -\frac{3}{4} \frac{\eta_{eff} + 2}{\eta_{eff}^3}, \quad (S28)$$

$$\frac{\partial \tilde{S}_l(r, \eta_{eff}[L_1])}{\partial \eta_{eff}} = \frac{e^{t_l(r-1)}}{t_l^3} [t_l^2(r^2 - r) - t_l(2r - 1) + 2] \frac{\partial t_l}{\partial \eta_{eff}}, \quad (S29)$$

$$\frac{\partial t_l}{\partial \eta_{eff}} = \frac{2[-1 + x_+j^l + x_-j^{-l}]}{(1 - \eta_{eff})^2} + \frac{2\eta_{eff}}{1 - \eta_{eff}} \left[\frac{\partial x_+}{\partial \eta_{eff}} j^l + \frac{\partial x_-}{\partial \eta_{eff}} j^{-l} \right], \quad (S30)$$

and

$$\frac{\partial K^{HS}}{\partial \eta} = - \left[\frac{1/\phi_0 + 1/\phi}{(1 - \eta/\phi_0)^2} + \frac{2\eta/\phi\phi_0}{(1 - \eta/\phi_0)^3} + a \frac{2\eta/\phi_0^2 + 1/\phi_0}{(1 - \eta/\phi_0)^4} + 4b \frac{\eta/\phi_0^2 + \eta^2/\phi_0^3}{(1 - \eta/\phi_0)^5} \right] (K^{HS})^2. \quad (S31)$$

Using above mentioned general relation (6) we calculate expressions for the pressure

$$\beta P_1 = -2\pi\beta\epsilon L_1^2 \left[G_{HS}(\eta_{eff}[L_1]) + \eta \frac{\partial \eta_{eff}}{\partial \eta} \frac{\partial G_{HS}(\eta_{eff}[L_1])}{\partial \eta_{eff}} \right], \quad (S32)$$

$$\begin{aligned} \beta P_2 = & -\pi\beta^2\epsilon^2 L_1^2 \left\{ G_{HS}(\eta_{eff}[L_1])\eta \frac{\partial K^{HS}}{\partial \eta} \right. \\ & \left. + K^{HS} \left[G_{HS}(\eta_{eff}[L_1]) + \eta \frac{\partial \eta_{eff}}{\partial \eta} \frac{\partial G_{HS}(\eta_{eff}[L_1])}{\partial \eta_{eff}} \right] \right\}. \end{aligned} \quad (S33)$$

Consequently, total chemical potential and pressure of the monomer contribution of SW segments in matrix are given by

$$\beta\mu^M(m) \equiv \beta\mu^{SW}(m) = \beta\mu_{HS}^{SPT2b1}(m) + \beta\mu_1(m) + \beta\mu_2(m), \quad (S34)$$

$$\beta P^M \equiv \beta P^{SW} = \beta P_{HS}^{SPT2b1} + \beta P_1 + \beta P_2. \quad (S35)$$

4 Chain contribution to thermodynamic properties

Similarly, as for thermodynamic properties of monomer contribution, differentiating the expression for Helmholtz free energy (17) with respect to the density and using general relation (6) we calculate expressions for chemical potential and pressure of chain contribution:

$$\begin{aligned} \beta\mu^{chain}(m) = & -(m-1) \ln(y^{SW}(\sigma, \eta_{eff}[L_1])) \\ & -(L_1 - L_0) \frac{m\pi\sigma^3}{6g^{SW}(\sigma, \eta_{eff}[L_1])} \frac{\partial g^{SW}(\sigma, \eta_{eff}[L_1])}{\partial \eta}, \end{aligned} \quad (S36)$$

$$\beta P^{chain} = -(L_1 - L_0) \frac{\eta}{g^{SW}(\sigma, \eta_{eff}[L_1])} \frac{\partial g^{SW}(\sigma, \eta_{eff}[L_1])}{\partial \eta}. \quad (S37)$$

The contact value of the monomer radial distribution function $g^{SW}(\sigma, \eta_{eff}[L_1])$ is obtained using expression (20):

$$\begin{aligned} g^{SW}(\sigma, \eta_{eff}[L_1]) = & g_{HS}(\sigma, \eta_{eff}[L_1]) + \beta\epsilon \left[\lambda^3 g_{HS}(\lambda\sigma, \eta_{eff}[L_1]) \right. \\ & \left. - \frac{3}{\sigma^3} \left\{ G_{HS}(\eta_{eff}[L_1]) + \eta \frac{\partial \eta_{eff}}{\partial \eta} \frac{\partial G_{HS}(\eta_{eff}[L_1])}{\partial \eta_{eff}} \right\} \right], \end{aligned} \quad (S38)$$

and for $\partial g^{SW}(\sigma, \eta_{eff}[L_1])/\partial \eta$ we have:

$$\begin{aligned} \frac{\partial g^{SW}(\sigma, \eta_{eff}[L_1])}{\partial \eta} &= \frac{\partial g_{HS}(\sigma, \eta_{eff}[L_1])}{\partial \eta_{eff}} \frac{\partial \eta_{eff}}{\partial \eta} + \beta \epsilon \left[\lambda^3 \frac{\partial g_{HS}(\lambda \sigma, \eta_{eff}[L_1])}{\partial \eta_{eff}} \frac{\partial \eta_{eff}}{\partial \eta} - \frac{3}{\sigma^3} \right. \\ &\times \left. \left\{ 2 \frac{\partial G_{HS}(\eta_{eff}[L_1])}{\partial \eta_{eff}} \frac{\partial \eta_{eff}}{\partial \eta} + \eta \left(\frac{\partial \eta_{eff}}{\partial \eta} \right)^2 \frac{\partial^2 G_{HS}(\eta_{eff}[L_1])}{\partial \eta_{eff}^2} + \eta \frac{\partial G_{HS}(\eta_{eff}[L_1])}{\partial \eta_{eff}} \frac{\partial^2 \eta_{eff}}{\partial \eta^2} \right\} \right]. \end{aligned} \quad (S39)$$

Here in the expressions (S38) and (S39) we substitute the relations obtained in the previous subsections. Also we have:

$$\begin{aligned} \frac{\partial g_{HS}(r, \eta_{eff}[L_1])}{\partial \eta_{eff}} &= \frac{1}{3r(1 - \eta_{eff})^2} \left\{ 6r(1 - \eta_{eff})g_{HS}(r, \eta_{eff}[L_1]) \right. \\ &+ \sum_{l=0}^2 \sum_{k=0}^2 j^{kl} \left[e^{t_l(r-1)} \frac{\partial H_k}{\partial \eta_{eff}} + H_k(r-1)e^{t_l(r-1)} \frac{\partial t_l}{\partial \eta_{eff}} \right] \Bigg\}, \end{aligned} \quad (S40)$$

$$\begin{aligned} \frac{\partial^2 \eta_{eff}}{\partial \eta^2} &= \left[\left(\frac{\partial g_{(HS)}^{(SPT)}(\sigma^+, \eta, \eta_0)}{\partial \eta} \right)^{-2} \frac{\partial^2 g_{(HS)}^{(SPT)}(\sigma^+, \eta, \eta_0)}{\partial \eta^2} \right. \\ &- \frac{2}{g_{(HS)}^{(SPT)}(\sigma^+, \eta, \eta_0)} \Bigg] \frac{\partial g_{(HS)}^{(SPT)}(\sigma^+, \eta, \eta_0)}{\partial \eta} \frac{\partial \eta_{eff}}{\partial \eta} + \frac{1}{g_{(HS)}^{(SPT)}(\sigma^+, \eta, \eta_0)} \\ &\times \left(\frac{\partial g_{(HS)}^{(SPT)}(\sigma^+, \eta, \eta_0)}{\partial \eta} \right)^2 \frac{36}{(1 + 24g_{(HS)}^{(SPT)}(\sigma^+, \eta, \eta_0))^{\frac{3}{2}}}, \end{aligned} \quad (S41)$$

$$\frac{\partial^2 g_{(HS)}^{(SPT)}(\sigma^+, \eta, \eta_0)}{\partial \eta^2} = \frac{8}{(\phi_0 - \eta)^3} + \frac{9(\eta + \eta_0 \tau)}{(\phi_0 - \eta)^4}, \quad (S42)$$

$$\begin{aligned} \frac{\partial^2 G_{HS}(\eta_{eff}[L_1])}{\partial \eta_{eff}^2} &= \frac{4}{1 - \eta_{eff}} \frac{\partial G_{HS}(\eta_{eff}[L_1])}{\partial \eta_{eff}} - \frac{1}{3(1 - \eta_{eff})^2} \left\{ 6G_{HS}(\eta_{eff}[L_1]) \right. \\ &- \sum_{l=0}^2 \sum_{k=0}^2 j^{kl} \left[\frac{\partial^2 H_k}{\partial \eta_{eff}^2} \Delta \tilde{S}_l(\eta_{eff}[L_1]) + 2 \frac{\partial H_k}{\partial \eta_{eff}} \frac{\partial \Delta \tilde{S}_l(\eta_{eff}[L_1])}{\partial \eta_{eff}} + H_k \frac{\partial^2 \Delta \tilde{S}_l(\eta_{eff}[L_1])}{\partial \eta_{eff}^2} \right] \Bigg\}, \end{aligned} \quad (S43)$$

$$\frac{\partial^2 H_0}{\partial \eta_{eff}^2} = 0, \quad (S44)$$

$$\begin{aligned} \frac{\partial^2 H_1}{\partial \eta_{eff}^2} = & - \left(\frac{1}{\eta_{eff}} + \frac{q}{q^2 + \frac{1}{8}} \frac{\partial q}{\partial \eta_{eff}} \right) \left\{ 2 \frac{\partial H_1}{\partial \eta_{eff}} + H_1 \left[\frac{1}{\eta_{eff}} + \frac{q}{q^2 + \frac{1}{8}} \frac{\partial q}{\partial \eta_{eff}} \right] \right\} \\ & - H_1 \left\{ \frac{1}{q^2 + \frac{1}{8}} \left[q \frac{\partial^2 q}{\partial \eta_{eff}^2} + \left(1 - \frac{2q^2}{q^2 + \frac{1}{8}} \right) \left(\frac{\partial q}{\partial \eta_{eff}} \right)^2 \right] - \frac{1}{\eta_{eff}^2} \right\} \\ & - \frac{1}{4\eta_{eff}} \frac{1}{\sqrt{q^2 + \frac{1}{8}}} \left\{ 2 \left(1 - 3\eta_{eff} - 4\eta_{eff}^2 \right) \left[\left(\frac{\partial x_-}{\partial \eta_{eff}} \right)^2 + x_- \frac{\partial^2 x_-}{\partial \eta_{eff}^2} \right] - 8x_-^2 \right. \\ & \left. - 4x_- (3 + 8\eta_{eff}) \frac{\partial x_-}{\partial \eta_{eff}} - 10\eta_{eff} \frac{\partial x_+}{\partial \eta_{eff}} + \left(1 - \frac{5}{2}\eta_{eff}^2 \right) \frac{\partial^2 x_+}{\partial \eta_{eff}^2} - 5x_+ \right\}, \quad (S45) \end{aligned}$$

$$\begin{aligned} \frac{\partial^2 H_2}{\partial \eta_{eff}^2} = & - \left(\frac{1}{\eta_{eff}} + \frac{q}{q^2 + \frac{1}{8}} \frac{\partial q}{\partial \eta_{eff}} \right) \left\{ 2 \frac{\partial H_2}{\partial \eta_{eff}} + H_2 \left[\frac{1}{\eta_{eff}} + \frac{q}{q^2 + \frac{1}{8}} \frac{\partial q}{\partial \eta_{eff}} \right] \right\} \\ & - H_2 \left\{ \frac{1}{q^2 + \frac{1}{8}} \left[q \frac{\partial^2 q}{\partial \eta_{eff}^2} + \left(1 - \frac{2q^2}{q^2 + \frac{1}{8}} \right) \left(\frac{\partial q}{\partial \eta_{eff}} \right)^2 \right] - \frac{1}{\eta_{eff}^2} \right\} \\ & + \frac{1}{4\eta_{eff}} \frac{1}{\sqrt{q^2 + \frac{1}{8}}} \left\{ 2 \left(1 - 3\eta_{eff} - 4\eta_{eff}^2 \right) \left[\left(\frac{\partial x_+}{\partial \eta_{eff}} \right)^2 + x_+ \frac{\partial^2 x_+}{\partial \eta_{eff}^2} \right] - 8x_+^2 \right. \\ & \left. - 4x_+ (3 + 8\eta_{eff}) \frac{\partial x_+}{\partial \eta_{eff}} - 10\eta_{eff} \frac{\partial x_-}{\partial \eta_{eff}} + \left(1 - \frac{5}{2}\eta_{eff}^2 \right) \frac{\partial^2 x_-}{\partial \eta_{eff}^2} - 5x_- \right\}, \quad (S46) \end{aligned}$$

$$\begin{aligned} \frac{\partial^2 x_{\pm}}{\partial \eta_{eff}^2} = & -\frac{2}{9} \left(q \pm \sqrt{q^2 + \frac{1}{8}} \right)^{-\frac{5}{3}} \left[1 \pm \frac{q}{\sqrt{q^2 + \frac{1}{8}}} \right]^2 \left(\frac{\partial q}{\partial \eta_{eff}} \right)^2 \\ & + \frac{1}{3} \left(q \pm \sqrt{q^2 + \frac{1}{8}} \right)^{-\frac{2}{3}} \left\{ \left[1 \pm \frac{q}{\sqrt{q^2 + \frac{1}{8}}} \right] \frac{\partial^2 q}{\partial \eta_{eff}^2} \pm \frac{1}{\sqrt{q^2 + \frac{1}{8}}} \left[1 - \frac{q^2}{q^2 + \frac{1}{8}} \right] \left(\frac{\partial q}{\partial \eta_{eff}} \right)^2 \right\} \quad (S47) \end{aligned}$$

$$\frac{\partial^2 q}{\partial \eta_{eff}^2} = \frac{3}{2} \frac{\eta_{eff} + 3}{\eta_{eff}^4}, \quad (S48)$$

$$\begin{aligned}
\frac{\partial^2 \tilde{S}_l(r, \eta_{eff}[L_1])}{\partial \eta_{eff}^2} &= \frac{e^{t_l(r-1)}}{t_l^3} [2t_l(r^2 - r) - 2r + 1] \left(\frac{\partial t_l}{\partial \eta_{eff}} \right)^2 \\
+ \left[\frac{\partial^2 t_l}{\partial \eta_{eff}^2} + \left(r - 1 - \frac{3}{t_l} \right) \left(\frac{\partial t_l}{\partial \eta_{eff}} \right)^2 \right] &\left(\frac{\partial t_l}{\partial \eta_{eff}} \right)^{-1} \frac{\partial \tilde{S}_l(r, \eta_{eff}[L_1])}{\partial \eta_{eff}}, \tag{S49}
\end{aligned}$$

$$\begin{aligned}
\frac{\partial^2 t_l}{\partial \eta_{eff}^2} &= \frac{4 [-1 + x_+ j^l + x_- j^{-l}]}{(1 - \eta_{eff})^3} + \frac{4}{(1 - \eta_{eff})^2} \left[\frac{\partial x_+}{\partial \eta_{eff}} j^l \right. \\
&\quad \left. + \frac{\partial x_-}{\partial \eta_{eff}} j^{-l} \right] + \frac{2\eta_{eff}}{1 - \eta_{eff}} \left[\frac{\partial^2 x_+}{\partial \eta_{eff}^2} j^l + \frac{\partial^2 x_-}{\partial \eta_{eff}^2} j^{-l} \right]. \tag{S50}
\end{aligned}$$

References

- (1) M. S. Wertheim, *Phys. Rev. Lett.*, 1963, **10**, 321-323.