Supporting Information to

Stochastic Analysis of Capillary Condensation in Disordered Mesopores

Derivation of Eq. (23)

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The specific surface area of the condensate free surface is related to the small-distance behavior of the covariance of the empty pore space $C_{OO}(r)$ via

$$C_{OO}(r) \simeq \phi_0 - \frac{\alpha_0}{4} r + O(r^2) \quad (SI-1)$$

From Eq. (20) of the main text, the covariance can be calculated as

$$C_{OO}(r) = \langle H[\beta = Y(x_1)] H[\gamma = Z(x_1)] H[\beta = Y(x_2)] H[\gamma = Z(x_2)] \rangle \quad (SI-2)$$

where the two points $x_1$ and $x_2$ are at distance $r$ from one another. This can be expressed in terms of the multivariate error function $\Lambda_4$, which can in principle be simplified using the same methods as used for $\Lambda_2$ and $\Lambda_3$ in Appendix A of the main text. However, the function $\Lambda_4$ depends in general on a total of ten arguments (four thresholds $\alpha$ and six correlations $g_{ij}$) so that the mathematics would be extremely cumbersome. We therefore consider here only the small-$r$ behavior of $C_{OO}$.

In Dirichlet’s representation, the step function $H[\cdot]$ is written as follows

$$H[y - \alpha] = \frac{-1}{2\pi i} \int_C dw e^{-i(y-\alpha)w} \quad (SI-3)$$

where the contour $C$ lies along the real axis but crosses the imaginary axis in upper half plane. Using Eq. (SI-3), the covariance function in Eq. (SI-2) can be written as

$$C_{OO}(r) = \left( \frac{-1}{2\pi i} \right)^4 \int_C dw_1 \int_C dw_2 \int_C dw'_1 \int_C dw'_2 e^{-i(w_1 \beta + w_2 \gamma + w'_1 \beta + w'_2 \gamma)} \langle e^{iw^T Y} \rangle \quad (SI-4)$$

where we have used the notations $w^T = [w_1 w'_1 w_2 w'_2]$ and $Y^T = [Y(x_1) Z(x_1) Y(x_2) Z(x_2)]$. The average value is calculated as

$$\langle e^{iw^T Y} \rangle = e^{-\frac{i}{2} w^T G w} \quad (SI-5)$$

where $G$ is the covariance matrix of $Y$ having the following structure

$$G = \begin{pmatrix} G(0) & \hat{G}(r) \\ \hat{G}(r) & G(0) \end{pmatrix} \quad \text{with} \quad \hat{G}(r) = \begin{pmatrix} \gamma(r) & \gamma Z(r) \\ \gamma Z(r) & g_z(r) \end{pmatrix} \quad (SI-6)$$

The only term proportional to $g_{YZ}(0)$ in the quadratic form $w^T G w$ being $2g_{YZ}(0)(w_1 w'_1 + w_2 w'_2)$, one can remove the singularity at $w_1 = w'_1 = 0$ (or at $w_2 = w'_2 = 0$) in Eq. (SI-4) by taking the derivative of $C_{OO}(r)$ with respect to $g_{YZ}(0)$. After some algebra this leads to

$$\frac{\partial C_{OO}(r)}{\partial g_{YZ}(0)} = -2 \left( \frac{-1}{2\pi i} \right)^4 \int_C \frac{dw_1}{w_2} \int_C \frac{dw'_1}{w'_2} e^{-i w_1 \beta - \frac{i}{2} w_1^2 \hat{G}(0) w_1} \int_C \frac{dw_2}{w_2} e^{-i w_2 \gamma - \frac{i}{2} w_2^2 \hat{G}(0) w_2}$$

$$-2 \left( \frac{-1}{2\pi i} \right)^4 \int_{-\infty}^{\infty} dw_1 \int_{-\infty}^{\infty} dw'_1 e^{-i w_1 \beta - \frac{i}{2} w_1^2 \hat{G}(0) w_1}$$

$$\int_{-\infty}^{\infty} dw_2 \int_{-\infty}^{\infty} dw'_2 e^{-i w_2 \gamma - \frac{i}{2} w_2^2 \hat{G}(0) w_2} \quad (SI-7)$$

with

$$\alpha^T = [\beta \gamma] \quad w^T_1 = [w_1 w'_1] \quad w^T_2 = [w_2 w'_2] \quad (SI-8)$$
\[ \chi = \alpha - i \mathbf{G}(r) w_2 \]  

The extra factor 2 in Eq. (SI-7) results from the symmetry of \( w^T \mathbf{G} w \) with respect to \( w_1 \) and \( w_2 \).

Removing the singularity in the contour integrals turns them into regular integrals along the real axis, which can be calculated using the general result

\[ \int_{-\infty}^{\infty} dw_1 \ldots \int_{-\infty}^{\infty} dw_n \ e^{-\frac{i}{2} w^T H w - i w^T z} = \frac{(2\pi)^{n/2}}{|H|^{1/2}} e^{-\frac{i}{2} z^T H^{-1} z} \]  

which holds for any symmetric and positive-definite matrix \( H \). Applying this formula to simplify Eq. (SI-7) leads to

\[ \frac{\partial C_{OO}(r)}{\partial g_Y Z(0)} = -\frac{1}{4\pi^3} \frac{1}{\vert \mathcal{G}(0) \vert^{1/2}} \exp \left( -\frac{\beta^2 + \gamma^2 - 2\beta \gamma g_Y Z(0)}{2(1 - g_Y Z(0))} \right) \]

\[ \times \Lambda_2 \left[ \left( -\mu_1 / \sqrt{h_1} \right), \left( -\mu_2 / \sqrt{h_2} \right), \left( h_{12} / \sqrt{h_1 h_2} \right), 1 \right] \]  

where \( \mu_{1/2} \) and \( h_{1/2/12} \) are the components of \( \mu \) and \( H \). The latter are obtained through Eq. (SI-12) via successive matrix multiplications; the values are

\[ \mu_1 = \beta - \frac{1}{1 - g_Y Z(0)} \left[ \beta [g_Y Z(0) g_Y Z(r)] + \gamma [g_Y Z(0) g_Y Z(r)] \right] \]  

\[ \mu_2 = \gamma - \frac{1}{1 - g_Y Z(0)} \left[ \beta [g_Y Z(0) g_Y Z(r)] + \gamma [g_Y Z(0) g_Y Z(r)] \right] \]  

and

\[ h_1 = 1 - \frac{1}{1 - g_Y Z(0)} \left[ g_Y^2(r) + g_Y^2 Z(0) - 2g_Y(r) g_Y Z(0) g_Y Z(r) \right] \]  

\[ h_2 = 1 - \frac{1}{1 - g_Y Z(0)} \left[ g_Y^2(r) + g_Y^2 Z(0) - 2g_Y(r) g_Y Z(0) g_Y Z(r) \right] \]  

\[ h_{12} = g_Y Z(0) - \frac{1}{1 - g_Y Z(0)} \left[ g_Y Z(r) [g_Y Z(r) + g_Y Z(r) - g_Y Z(0) [g_Y Z(r) g_Y Z(r) + g_Y^2 Z(r)] \right] \]  

The partial derivative \( \partial C_{OO}/\partial g_Y Z(r) \) can be calculated along the same lines as Eq. (SI-13). This leads to the following expression

\[ \frac{\partial C_{OO}(r)}{\partial g_Y Z(r)} = \frac{1}{\pi \sqrt{1 - g_Y Z(r)}} \exp \left( -\frac{\beta^2 + \gamma^2 - 2\beta \gamma g_Y Z(r)}{2(1 - g_Y Z(r))} \right) \]

\[ \times \Lambda_2 \left[ \left( -\mu'_1 / \sqrt{h'_1} \right), \left( -\mu'_2 / \sqrt{h'_2} \right), \left( h'_{12} / \sqrt{h'_1 h'_2} \right), 1 \right] \]  

where \( \mu'_{1/2} \) and \( h'_{1/2/12} \) are obtained from Eqs. (SI-14), (SI-15), (SI-16), (SI-17) and (SI-18) by replacing \( g_Y Z(0) \) with \( g_Y Z(r) \) and vice versa.
The function $C_{OO}(r)$ can be viewed as being defined in a 4-dimensional parameter space, with dimensions $g_Y(r)$, $g_Z(r)$, $g_{YZ}(0)$ and $g_{YZ}(r)$. Knowing the two partial derivatives $\partial C_{OO}(r)/\partial g_{YZ}(0)$ and $\partial C_{OO}(r)/\partial g_{YZ}(r)$ enables one to calculate the value of $C_{OO}(r)$ via a path integral in the corresponding $[g_{YZ}(0), g_{YZ}(r)]$ plane. In order to formalize this, we note that Eqs. (SI-13) and (SI-19) have the structure

\[
\text{Introducing these expressions in Eq. (SI-13) leads to}
\]

\[
\frac{\partial C_{OO}}{\partial x} = f(x, y) \quad \text{and} \quad \frac{\partial C_{OO}}{\partial y} = f(y, x)
\]

\[(\text{SI-20)}\]

where $x$ stands for $g_Y(0)$ and $y$ for $g_{YZ}(r)$. A natural choice for the path along which to integrate is the straight line joining the points $[x = 0; y = 0]$ and $[x = g_Y(0); y = g_{YZ}(r)]$, which can be parametrized as

\[
x = t g_Y(0) \quad y = t g_{YZ}(r)
\]

\[(\text{SI-21)}\]

where $t$ is an integration variable that takes values between 0 and 1. Evaluating the path integral along this straight line leads to

\[
C_{OO}(r) = C_{OO}(r) \bigg|_0 + g_{YZ}(0) \int_0^1 f(t g_Y(0), t g_{YZ}(r)) \, dt + g_{YZ}(r) \int_0^1 f(t g_Y(0), t g_{YZ}(r)) \, dt
\]

\[(\text{SI-22)}\]

The starting point of the path, $C_{OO}(r) \bigg|_0$, corresponds to the situation where $g_{YZ}(r) = 0$ for all $r$, which means that the fields Y and Z are independent. In this case the two-point function takes the value

\[
C_{OO}(r) \bigg|_0 = \left\{ \begin{array}{l}
1 - 2 \Lambda_1 [\beta] + \Lambda_2 \left[ \left( \begin{array}{c}
\beta \\
\gamma
\end{array} \right), \left( \begin{array}{c}
g_Y(r) \\
g_{YZ}(r)
\end{array} \right) \right] \\
\times \left[ \begin{array}{l}
1 - 2 \Lambda_1 [\gamma] + \Lambda_2 \left[ \left( \begin{array}{c}
\gamma \\
\beta
\end{array} \right), \left( \begin{array}{c}
g_Z(r) \\
g_{YZ}(r)
\end{array} \right) \right]
\end{array} \right]
\end{array} \right\}
\]

\[(\text{SI-23)}\]

which results directly from Eq. (SI-2) if the fields Y and Z are independent from one another.

The specific surface area $a_O$ then obtained from Eq. (SI-1). For small values of $r$ the field correlation functions are quadratic, and their expressions are given by Eq. (4), (B8) and (B10) of the main text. Using these expressions in Eqs. (SI-14), (SI-15), (SI-16), (SI-17) and (SI-18), and neglecting all contributions of order $O(r^3)$, one obtains

\[
\frac{\mu_1}{\sqrt{h_1}} = \frac{\nu_1 r}{\sqrt{2l_Y}} \quad \frac{\mu_2}{\sqrt{h_2}} = \frac{\nu_2 r}{\sqrt{2l_Z}} \quad \frac{h_{12}}{\sqrt{h_1 h_2}} = \frac{g_{YZ}(0) l_Y l_Z}{l_{YZ}}
\]

\[(\text{SI-24)}\]

with

\[
\nu_1 = \beta + \frac{(\beta g_Y(0) - \gamma) g_{YZ}(0)}{1 - g_{YZ}(0)} \left[ 1 - \left( \frac{l_Y}{l_{YZ}} \right)^2 \right]
\]

\[(\text{SI-25)}\]

and

\[
\nu_2 = \gamma + \frac{(\gamma g_Y(0) - \beta) g_{YZ}(0)}{1 - g_{YZ}(0)} \left[ 1 - \left( \frac{l_Z}{l_{YZ}} \right)^2 \right]
\]

\[(\text{SI-26)}\]

Introducing these expressions in Eq. (SI-13) leads to

\[
\frac{\partial C_{OO}}{\partial g_{YZ}(0)} = \frac{1}{\pi \sqrt{1 - g_{12}(0)^2}} \exp \left( -\frac{\beta^2 + \gamma^2 - 2 \beta \gamma g_{YZ}(0)}{2(1 - g_{YZ}(0))^2} \right) \times \left\{ \begin{array}{l}
\frac{1}{4} + \frac{1}{4 \pi} \left( \frac{\nu_1}{l_Y} + \frac{\nu_2}{l_Z} \right) + \frac{1}{2 \pi} \arcsin \left( g_{YZ}(0) \frac{l_Y l_Z}{l_{YZ}} \right) \\
+ O(r^2)
\end{array} \right\}
\]

\[(\text{SI-27)}\]

If we proceed in the same way for Eq. (SI-19), i.e. starting with Eqs Eqs. (SI-14), (SI-15), (SI-16), (SI-17) and (SI-18) with $g_{YZ}(0)$ exchanged with $g_{YZ}(r)$, this eventually leads to

\[
\frac{\mu_1'}{\sqrt{h_1}} = \frac{\nu_1' r}{\sqrt{2l_Y}} \quad \frac{\mu_2'}{\sqrt{h_2}} = \frac{\nu_2' r}{\sqrt{2l_Z}} \quad \frac{h_{12}'}{\sqrt{h_1 h_2}} = \frac{-g_{12}(0) l_Y l_Z}{l_{YZ}}
\]

\[(\text{SI-28)}\]
with

\[ \nu'_1 = \beta + \frac{(\beta g_{YZ}(0) - \gamma)g_{YZ}(0)}{1 - g_{YZ}^2(0)} \left[ 1 + \left( \frac{l_Y}{l_{YZ}} \right)^2 \right] \]  
(SI-29)

and

\[ \nu'_2 = \gamma + \frac{\gamma g_{YZ}(0) - \beta g_{YZ}(0)}{1 - g_{YZ}^2(0)} \left[ 1 + \left( \frac{l_Z}{l_{YZ}} \right)^2 \right] \]  
(SI-30)

We finally obtain

\[
\frac{\partial C_{OO}}{\partial g_{YZ}(r)} = \frac{1}{\pi \sqrt{1 - g_{YZ}^2(0)}} \exp \left( -\frac{\beta^2 + \gamma^2 - 2\beta\gamma g_{YZ}(0)}{2(1 - g_{YZ}^2(0))} \right) \\
\times \left\{ \frac{1}{4} + \frac{1}{4\sqrt{\pi}} \left( \frac{\nu'_1}{l_Y} + \frac{\nu'_2}{l_Y} \right) - \frac{1}{2\pi} \arcsin \left( g_{YZ}(0) \frac{l_Y l_Z}{l_{YZ}} \right) \right\} + O(r^2) 
\]  
(SI-31)

If one introduces Eqs. (SI-27) and (SI-31) into Eq. (SI-22), one eventually finds Eq. (SI-1) with \( \phi_O \) and \( a_O \) given by Eqs. (21) and (23) of the main text, respectively.