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

$$C_{OO}(r) \simeq \phi_O - \frac{a_O}{4} r + O(r^2) \tag{SI-1}$$

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

$$C_{OO}(r) = \langle H[\beta - Y(\mathbf{x}_1)] H[\gamma - Z(\mathbf{x}_1)] H[\beta - Y(\mathbf{x}_2)] H[\gamma - Z(\mathbf{x}_2)] \rangle \tag{SI-2}$$

where the two points $\mathbf{x}_1$ and $\mathbf{x}_2$ are at distance r from one another. This can be expressed in terms of the multivariate error function Λ_4, which can in principle be simplified using the same methods as used for Λ_2 and Λ_3 in Appendix A of the main text. However, the function Λ_4 depends in general on a total of ten arguments (four thresholds α 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 $H[.]$ is written as follows

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

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

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

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

$$\left\langle e^{i\mathbf{w}^T \cdot \mathbf{y}} \right\rangle = e^{-\frac{1}{2}\mathbf{w}^T \mathbf{G} \mathbf{w}} \tag{SI-5}$$

where $\mathbf{G}$ is the covariance matrix of $\mathbf{Y}$ having the following structure

$$\mathbf{G} = \begin{pmatrix} \hat{\mathbf{G}}(0) & \hat{\mathbf{G}}(r) \\ \hat{\mathbf{G}}(r) & \hat{\mathbf{G}}(0) \end{pmatrix} \quad \text{with} \quad \hat{\mathbf{G}}(r) = \begin{pmatrix} g_Y(r) & g_{YZ}(r) \\ g_{YZ}(r) & g_Z(r) \end{pmatrix} \tag{SI-6}$$

The only term proportional to $g_{YZ}(0)$ in the quadratic form $\mathbf{w}^T\mathbf{G}\mathbf{w}$ being $2g_{YZ}(0)(w_1w_1' + w_2w_2')$, 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

$$\frac{\partial C_{OO}(r)}{\partial g_{YZ}(0)} = -2\left(\frac{-1}{2i\pi}\right)^4 \int_C \frac{dw_2}{w_2} \int_C \frac{dw_2'}{w_2'} e^{-i\mathbf{w}_2^T \cdot \alpha - \frac{1}{2}\mathbf{w}_2^T \hat{\mathbf{G}}(0)\mathbf{w}_2} \int_{-\infty}^{\infty} dw_1 \int_{-\infty}^{\infty} dw_1'\, e^{-i\mathbf{w}_1^T \cdot \chi - \frac{1}{2}\mathbf{w}_1^T \hat{\mathbf{G}}(0)\mathbf{w}_1} \tag{SI-7}$$

with

$$\alpha^T = [\beta\ \gamma]\ , \quad \mathbf{w}_1^T = [w_1\ w_1']\ , \quad \mathbf{w}_2^T = [w_2\ w_2'] \tag{SI-8}$$

and

$$\chi = \alpha - i\hat{\mathbf{G}}(r)\mathbf{w}_2 \tag{SI-9}$$

The extra factor 2 in Eq. (SI-7) results from the symmetry of $\mathbf{w}^T\mathbf{G}\mathbf{w}$ with respect to $\mathbf{w}_1$ and $\mathbf{w}_2$.

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

$$\int_{-\infty}^{+\infty} dw_1 \ldots \int_{-\infty}^{+\infty} dw_n \quad e^{-\frac{1}{2}\mathbf{w}^T\mathbf{H}\mathbf{w} - i\mathbf{w}^T\cdot\mathbf{z}} = \frac{(2\pi)^{n/2}}{|\mathbf{H}|^{1/2}} e^{-\frac{1}{2}\mathbf{z}^T\mathbf{H}^{-1}\mathbf{z}} \tag{SI-10}$$

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

$$\frac{\partial C_{OO}(r)}{\partial g_{YZ}(0)} = \frac{-1}{4\pi^3}\frac{1}{|\hat{G}(0)|^{1/2}} \; e^{-\frac{1}{2}\alpha^T\hat{\mathbf{G}}^{-1}(0)\alpha} \int_C \frac{dw_2}{w_2}\int_C \frac{dw_2'}{w_2'} \; e^{-i\mathbf{w}_2^T\cdot\mu - \frac{1}{2}\mathbf{w}_2^T\mathbf{H}\mathbf{w}_2} \tag{SI-11}$$

with

$$\mu = \alpha - \hat{\mathbf{G}}(r)\hat{\mathbf{G}}^{-1}(0)\alpha \quad \text{and} \quad \mathbf{H} = \hat{\mathbf{G}}(0) - \hat{\mathbf{G}}(r)\hat{\mathbf{G}}^{-1}(0)\hat{\mathbf{G}}(r) \tag{SI-12}$$

The double contour integral in Eq. (SI-11) can be conveniently expressed in terms of Λ_2. This eventually leads to the following final expression

$$\begin{aligned}\frac{\partial C_{OO}(r)}{\partial g_{YZ}(0)} &= \frac{1}{\pi\sqrt{1-g_{YZ}^2(0)}} \exp\left(-\frac{\beta^2+\gamma^2-2\beta\gamma g_{YZ}(0)}{2(1-g_{YZ}^2(0))}\right) \\ &\times \Lambda_2\left[\begin{pmatrix} -\mu_1/\sqrt{h_1} \\ -\mu_2/\sqrt{h_2}\end{pmatrix}, \begin{pmatrix} 1 & h_{12}/\sqrt{h_1h_2} \\ h_{12}/\sqrt{h_1h_2} & 1\end{pmatrix}\right]\end{aligned} \tag{SI-13}$$

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

$$\mu_1 = \beta - \frac{1}{1-g_{YZ}^2(0)}\Big[\beta\left[g_Y(r) - g_{YZ}(0)g_{YZ}(r)\right] + \gamma\left[g_{YZ}(r) - g_Y(r)g_{YZ}(0)\right]\Big] \tag{SI-14}$$

$$\mu_2 = \gamma - \frac{1}{1-g_{YZ}^2(0)}\Big[\beta\left[g_{YZ}(r) - g_Z(r)g_{YZ}(0)\right] + \gamma\left[g_Z(r) - g_{YZ}(0)g_{YZ}(r)\right]\Big] \tag{SI-15}$$

and

$$h_1 = 1 - \frac{1}{1-g_{YZ}^2(0)}\Big[g_Y^2(r) + g_{YZ}^2(r) - 2g_Y(r)g_{YZ}(0)g_{YZ}(r)\Big] \tag{SI-16}$$

$$h_2 = 1 - \frac{1}{1-g_{YZ}^2(0)}\Big[g_Z^2(r) + g_{YZ}^2(r) - 2g_Z(r)g_{YZ}(0)g_{YZ}(r)\Big] \tag{SI-17}$$

$$h_{12} = g_{YZ}(0) - \frac{1}{1-g_{YZ}^2(0)}\Big[g_{YZ}(r)\left[g_Y(r)+g_Z(r)\right] - g_{YZ}(0)\left[g_Y(r)g_Z(r) + g_{YZ}^2(r)\right]\Big] \tag{SI-18}$$

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

$$\begin{aligned}\frac{\partial C_{OO}(r)}{\partial g_{YZ}(r)} &= \frac{1}{\pi\sqrt{1-g_{YZ}^2(r)}} \exp\left(-\frac{\beta^2+\gamma^2-2\beta\gamma\, g_{YZ}(r)}{2(1-g_{YZ}^2(r))}\right) \\ &\times \Lambda_2\left[\begin{pmatrix} -\mu_1'/\sqrt{h_1'} \\ -\mu_2'/\sqrt{h_2'}\end{pmatrix}, \begin{pmatrix} 1 & h_{12}'/\sqrt{h_1'h_2'} \\ h_{12}'/\sqrt{h_1'h_2'} & 1\end{pmatrix}\right]\end{aligned} \tag{SI-19}$$

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 $g_{YZ}(0)$ with $g_{YZ}(r)$ 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

$$\frac{\partial C_{OO}}{\partial x} = f(x,y) \quad \text{and} \quad \frac{\partial C_{OO}}{\partial y} = f(y,x) \tag{SI-20}$$

where x stands for $g_{YZ}(0)$ 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 $[x=g_{YZ}(0); y=g_{YZ}(r)]$, which can be parametrized as

$$x = t g_{YZ}(0) \quad y = t g_{YZ}(r) \tag{SI-21}$$

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

$$C_{OO}(r) = C_{OO}(r)\Big|_0 + g_{YZ}(0)\int_0^1 f(tg_{YZ}(0), tg_{YZ}(r))\,dt + g_{YZ}(r)\int_0^1 f(tg_{YZ}(r), tg_{YZ}(0))\,dt \tag{SI-22}$$

The starting point of the path, $C_{OO}(r)\Big|_0$, 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

$$\begin{aligned} C_{OO}(r)\Big|_0 = &\left\{1 - 2\Lambda_1[\beta] + \Lambda_2\left[\begin{pmatrix}\beta\\ \beta\end{pmatrix}, \begin{pmatrix}1 & g_Y(r)\\ g_Y(r) & 1\end{pmatrix}\right]\right\} \\ &\times\left\{1 - 2\Lambda_1[\gamma] + \Lambda_2\left[\begin{pmatrix}\gamma\\ \gamma\end{pmatrix}, \begin{pmatrix}1 & g_Z(r)\\ g_Z(r) & 1\end{pmatrix}\right]\right\} \end{aligned} \tag{SI-23}$$

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

$$\frac{\mu_1}{\sqrt{h_1}} = \frac{\nu_1 r}{\sqrt{2} l_Y} \quad \frac{\mu_2}{\sqrt{h_2}} = \frac{\nu_2 r}{\sqrt{2} l_Z} \quad \frac{h_{12}}{\sqrt{h_1 h_2}} = g_{YZ}(0)\frac{l_Y l_Z}{l_{YZ}} \tag{SI-24}$$

with

$$\nu_1 = \beta + \frac{(\beta g_{YZ}(0) - \gamma) g_{YZ}(0)}{1 - g_{YZ}^2(0)}\left[1 - \left(\frac{l_Y}{l_{YZ}}\right)^2\right] \tag{SI-25}$$

and

$$\nu_2 = \gamma + \frac{(\gamma g_{YZ}(0) - \beta) g_{YZ}(0)}{1 - g_{YZ}^2(0)}\left[1 - \left(\frac{l_Z}{l_{YZ}}\right)^2\right] \tag{SI-26}$$

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

$$\begin{aligned} \frac{\partial C_{OO}}{\partial g_{YZ}(0)} = &\frac{1}{\pi\sqrt{1 - g_{12}^2(0)}}\exp\left(-\frac{\beta^2 + \gamma^2 - 2\beta\gamma g_{YZ}(0)}{2(1 - g_{YZ}^2(0))}\right) \\ &\times\left\{\frac{1}{4} + \frac{1}{4\sqrt{\pi}}\left(\frac{\nu_1}{l_Y} + \frac{\nu_2}{l_Z}\right) + \frac{1}{2\pi}\arcsin\left(g_{YZ}(0)\frac{l_Y l_Z}{l_{YZ}}\right)\right\} + O(r^2) \end{aligned} \tag{SI-27}$$

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

$$\frac{\mu_1'}{\sqrt{h_1'}} = \frac{\nu_1' r}{\sqrt{2} l_Y} \quad \frac{\mu_2'}{\sqrt{h_2'}} = \frac{\nu_2' r}{\sqrt{2} l_Z} \quad \frac{h_{12}'}{\sqrt{h_1' h_2'}} = -g_{12}(0)\frac{l_Y l_Z}{l_{YZ}} \tag{SI-28}$$

with

$$\nu_1' = \beta + \frac{(\beta g_{YZ}(0) - \gamma) g_{YZ}(0)}{1 - g_{YZ}^2(0)} \left[1 + \left(\frac{l_Y}{l_{YZ}} \right)^2 \right] \tag{SI-29}$$

and

$$\nu_2' = \gamma + \frac{(\gamma g_{YZ}(0) - \beta) g_{YZ}(0)}{1 - g_{YZ}^2(0)} \left[1 + \left(\frac{l_Z}{l_{YZ}} \right)^2 \right] \tag{SI-30}$$

We finally obtain

$$\begin{aligned} \frac{\partial C_{OO}}{\partial g_{YZ}(r)} &= \frac{1}{\pi \sqrt{1 - g_{YZ}^2(0)}} \exp\left(-\frac{\beta^2 + \gamma^2 - 2\beta\gamma g_{YZ}(0)}{2(1 - g_{YZ}^2(0))} \right) \\ &\times \left\{ \frac{1}{4} + \frac{1}{4\sqrt{\pi}} \left(\frac{\nu_1'}{l_Y} + \frac{\nu_2'}{l_Y} \right) - \frac{1}{2\pi} \arcsin\left(g_{YZ}(0) \frac{l_Y l_Z}{l_{YZ}} \right) \right\} + O(r^2) \end{aligned} \tag{SI-31}$$

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