Supporting Information: Compressing Θ-chain in slit geometry

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The second virial coefficient of Lennard Jones particles in slit confinement

The second virial coefficient for hard-sphere (HS) system amounts to the volume of a spherical particle inaccessible to others. That is, the second virial coefficient for homogeneous hard sphere system with diameter a, $B_2^{\rm HS} = \frac{1}{2}\int d\mathbf{r}(1 - e^{-u(\mathbf{r})/k_BT})$ with $u(\mathbf{r}) = \infty$ for $r < a$ and 0 for $r \geq a$ is given as $B_2^{\rm HS} = (2\pi/3)a^3$. Geometrical confinement may be regarded as an external field applied to the particles, and it modifies the spatial distribution of a particle at $\mathbf{r}$ with a factor $g(\mathbf{r}) \sim e^{-\beta E(\mathbf{r})}$, where $E(\mathbf{r})$ is the potential energy that the particle experiences in the presence of the external field. The second virial coefficient of hard sphere system in slit confinement is given as[1]

$$B_2 = -\frac{V}{2}\frac{\int d\mathbf{r}_1 g(\mathbf{r}_1)\int d\mathbf{r}_2 g(\mathbf{r}_2) f(\mathbf{r}_1,\mathbf{r}_2)}{\int d\mathbf{r}_1 g(\mathbf{r}_1)\int d\mathbf{r}_2 g(\mathbf{r}_2)}. \tag{S1}$$

In this expression, the Mayer function is $f(\mathbf{r}_1,\mathbf{r}_2) = e^{-\beta u(r_{12})} - 1 = H(|r_1 - r_2| - a) - 1$ for hard spheres where $H(\ldots)$ is the Heaviside step function. The integral $g(\mathbf{r}_1)\int d\mathbf{r}_2 g(\mathbf{r}_2) f(\mathbf{r}_1,\mathbf{r}_2)$ corresponds to the volume around a particle at $\mathbf{r}_1$ that is inaccessible to other particles under the constraint that all the particles are confined between the slit. The integral $\int d\mathbf{r} g(\mathbf{r}) = A(D-a)$ denotes the volume accessible for a sphere of diameter a inside the slit of width D and area A. Since the inaccessible volume around the particle varies with its location along the z axis, B_2 can be written in the following form.

$$B_2(D) = \frac{AD}{2}\frac{A\int_{-D/2+a/2}^{D/2-a/2} dz V(z)}{A^2(D-a)^2} \tag{S2}$$

Next, in order to evaluate the second virial coefficient, a system of Lennard-Jones particles may be approximated by a square well potential of depth ϵ and width δ (see Fig.**??**A). In free space, the inaccessible volume calculated above for hard sphere system is adjusted by a factor $\psi(\epsilon,\delta)$ as

$$\begin{aligned}\int d\mathbf{r}(1 - e^{-\beta u(\mathbf{r})}) &= 4\pi\int_0^a r^2 dr + 4\pi\int_a^{a+\delta} r^2 dr(1 - e^{\beta\epsilon}) \\ &= \frac{4\pi}{3}a^3 \underbrace{\left[1 + (1 - e^{\beta\epsilon})\left(\left(1 + \frac{\delta}{a}\right)^3 - 1\right)\right]}_{\equiv\psi(\epsilon,\delta)}\end{aligned} \tag{S3}$$

The effective volume element $V(z)$ for LJ in Eq.S2 is calculated as (see Fig. 4B):

(i) $a \le D \le 2a$,

$$V_{\rm LJ}^{<}(z) = \pi \int_{-\frac{D}{2}+\frac{a}{2}-z}^{\frac{D}{2}-\frac{a}{2}-z} dy(a^2 - y^2) + \pi(1 - e^{\beta\epsilon}) \int_{-\frac{D}{2}+\frac{a}{2}-z}^{\frac{D}{2}-\frac{a}{2}-z} dy \left[(a+\delta)^2 - y^2\right]$$
$$- \pi(1 - e^{\beta\epsilon}) \int_{-\frac{D}{2}+\frac{a}{2}-z}^{\frac{D}{2}-\frac{a}{2}-z} dy(a^2 - y^2)$$

(ii) $D \ge 2a$,

- For $\frac{D}{2} - \frac{3a}{2} \le z \le \frac{D}{2} - \frac{a}{2}$

$$V_{\rm LJ}^{>,1}(z) = \pi e^{\beta\epsilon} \int_{-a}^{D/2-a/2-z} dy(a^2 - y^2) + \pi(1 - e^{\beta\epsilon}) \int_{-(a+\delta)}^{D/2-a/2-z} dy((a+\delta)^2 - y^2)$$

- For $-\frac{D}{2} + \frac{3a}{2} \le z \le \frac{D}{2} - \frac{3a}{2}$

$$\begin{aligned} V_{\rm LJ}^{>,2}(z) &= \pi e^{\beta\epsilon} \int_{-a}^{a} dy(a^2 - y^2) + \pi(1 - e^{\beta\epsilon}) \int_{-a-\delta}^{a+\delta} dy((a+\delta)^2 - y^2) \\ &= \frac{4\pi}{3} a^3 \psi(\epsilon, \delta) \end{aligned}$$

- For $-\frac{D}{2} + \frac{a}{2} \le z \le -\frac{D}{2} + \frac{3a}{2}$

$$V_{\rm LJ}^{>,3}(z) = \pi e^{\beta\epsilon} \int_{-D/2+a/2-z}^{a} dy(a^2 - y^2) + \pi(1 - e^{\beta\epsilon}) \int_{-D/2+a/2-z}^{a+\delta} dy((a+\delta)^2 - y^2)$$

Then, $B_2(D)$ for LJ systems is obtained by calculating $B_2^{\rm LJ}(D) = \frac{D}{2(D-a)^2} \int_{-D/2+a/2}^{D/2-a/2} V_{\rm LJ}(z) dz$.

Eq.S2 is evaluated with the explicit forms of $V_{\rm LJ}^{<}(z)$ and $V_{\rm LJ}^{>,i}(z)$ given above:

(i) For $a \leq D \leq 2a$

$$B_2^{\rm LJ}(D) = \frac{D}{2(D-a)^2}\int_{-D/2+a/2}^{D/2-a/2} dz V_{\rm LJ}^{<}(z) \tag{S4}$$

(ii) For $D \geq 2a$

$$B_2^{\rm LJ}(D) = \frac{D}{2(D-a)^2}\left(\int_{-D/2+a/2}^{-D/2+3a/2} dz V_{\rm LJ}^{>,1}(z) + \int_{-D/2+3a/2}^{D/2-3a/2} V_{\rm LJ}^{>,2}(z)dz + \int_{D/2-3a/2}^{D/2-a/2} V_{\rm LJ}^{>,3}(z)dz\right) \tag{S5}$$

These enable obtaining the expression given in Eq. 20.

The condition of either $\psi(\epsilon,\delta) \to 1$ ($\epsilon = 0$ or $e^{\beta\epsilon} = 1$) or $\delta/a = 0$ reduces the second virial coefficient of LJ system into that of hard-sphere systems:[2]

$$B_2^{\rm LJ}(D) \to B_2^{\rm HS}(D) = \begin{cases} \frac{\pi a^3(D/a)}{2}\left[\frac{5}{6} + \frac{1}{3}\frac{D}{a} - \frac{1}{6}\left(\frac{D}{a}\right)^2\right] & (a < D \leq 2a), \\ \frac{\pi a^3(D/a)}{2(D/a-1)^2}\left[\frac{4}{3}\frac{D}{a} - \frac{11}{6}\right] & (D \geq 2a). \end{cases} \tag{S6}$$

$B_2^{\rm HS}(D)$ changes its value from $B_2^{\rm HS}(D \to \infty) = (2\pi/3)a^3$ in free space to $B_2^{\rm HS}(D \to a) = (\pi/2)a^3$ in tightly confined space. It is interesting to note that both $B_2^{\rm HS}(D)$ and $B_2^{\rm LJ}(D)$ display non-monotonic variation with D, maximized at $D \approx 2a$ (see black curve in Fig. 4C).

References

(1) Krekelberg, W. P.; Mahynski, N. A.; Shen, V. K. *J. Chem. Phys.* **2019**, *150*, 044704.

(2) Yang, J. H.; Schultz, A. J.; Errington, J. R.; Kofke, D. A. *Mol. Phys.* **2015**, *113*, 1179–1189.