ANALYTICAL THEORY OF POLYMER-NETWORK MEDIATED INTERACTION BETWEEN COLLOIDAL PARTICLES: SUPPLEMENTARY INFORMATION

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1. Estimation of the effective interaction between a single acrylamide monomer and a silica colloid surface

A single acrylamide monomer of size b interacts with a silica colloid of diameter σ via van der Waals (vdW) forces. Assuming $b \ll \sigma$, the problem reduces to the interaction between a single acrylamide molecule and a flat silica surface, both immersed in water [1]

$$V_{\mathrm{mono}}^{\mathrm{single}}(z) = -\frac{Ab^3}{3z^3} \tag{1}$$

where z is the distance between the surface of the colloid and the monomer. $A \approx 10^{-20}$J is the Hamaker constant that depends on the relative dielectric constant of silica (ϵ_{s}), acrylamide (ϵ_{A}) and water (ϵ_{w}) according to the relation [1]

$$A \propto \frac{(\epsilon_{\mathrm{A}} - \epsilon_{\mathrm{w}})(\epsilon_{\mathrm{s}} - \epsilon_{\mathrm{w}})}{(\epsilon_{\mathrm{A}} + \epsilon_{\mathrm{w}})(\epsilon_{\mathrm{s}} + \epsilon_{\mathrm{w}})}. \tag{2}$$

If we consider a single acrylamide monomer immersed in a solution of identical monomers, ϵ_{w} must be replaced with an effective dielectric constant that depends on the volume fraction f of acrylamide monomers $\tilde{\epsilon}_{\mathrm{w}} = f\epsilon_{\mathrm{A}} + (1-f)\epsilon_{\mathrm{w}}$. For the case $f \to 1$ (high monomer density) $A \propto (\epsilon_{\mathrm{A}} - \epsilon_{\mathrm{w}})(1-f) \to 0$, thus the vdW interaction would be screened in dense acrylamide solutions. When a polyacrylamide polymer is adsorbed onto the colloid per effect of vdW, a dense layer of monomer will accumulate in contact with the colloid.

The vdW forces will thus be screened for all the monomers except for those in contact with colloid surface and can be modeled as:

$$V_z = \begin{cases} +\infty & \text{if } z < 0 \\ -\delta\ k_{\mathrm{B}}T & \text{if } 0 \le z < d \\ 0 & \text{if } z \ge \delta \end{cases} \tag{3}$$

where $-\delta\ k_{\mathrm{B}}T$ and d are the energy and the depth of the effective monomer-wall interaction and are simply related by

$$-\delta\ k_{\mathrm{B}}T = \frac{Ab^3}{3d^3}. \tag{4}$$

d should be taken as the distance between the silica wall and an adsorbed monomer in contact with it and A should be an appropriate Hamaker constant. Both silica and acrylamide are hydrophilic, thus a layer of water molecules of thickness h will always be present between an adsorbed monomer and the silica. We can take $A \approx 10^{-20}$ J, as for the silica–water–acrylamide system and $d \approx b/2 + h$.
Knowing that $b \approx 0.5$ nm and $h \approx 0.5 - 1$ nm [2] we have $\delta \approx 0.1$ (assuming $h = 0.75$ nm).

2. Force between two colloidal particles partially embedded in a polymer network

In this derivation, initially we follow closely references [3, 4]. Consider a binary mixture of big hard spheres (species 1) of diameter σ that we identify with the colloids and small ones (species 2) that we identify with the polymer blobs. The interaction potential between the two species is:

$$V_{\mathrm{bc}}(r) = \begin{cases} +\infty & \text{if } r \le \sigma_{\mathrm{bc}} \\ -\epsilon & \text{if } \sigma_{\mathrm{bc}} < r \le \lambda\sigma_{\mathrm{bc}} \\ 0 & \text{if } r > \lambda\sigma_{\mathrm{bc}} \end{cases} \tag{5}$$

In relation to our model, we have $\sigma_{\mathrm{bc}} = R_{\mathrm{F}}/2 + \xi_{\mathrm{ads}}/4$ and $\lambda\sigma_{\mathrm{bc}} = R_{\mathrm{F}}/2 + \xi_{\mathrm{ads}}/2 = \sigma_{\mathrm{bc}} + \xi_{\mathrm{ads}}/4$ (see main text for definitions). The force $f(R)$ between two big spheres with center–to–center distance R can be written as:

$$f(R) = -\frac{\partial\varphi_{11}}{\partial R} - \frac{\partial \mathrm{F}_2}{\partial R} = -\frac{\partial\varphi_{11}}{\partial R} + \frac{1}{\beta \mathrm{Z}_2}\frac{\partial \mathrm{Z}_2}{\partial R} \tag{6}$$

where φ_{11} is the interaction potential between species 1 particles, i.e. hard sphere repulsion, F_2 is the free energy of species 2 particles, Z_2 is the corresponding partition function and $\beta = 1/k_{\mathrm{B}}T$. We can write:

$$\frac{\partial \mathrm{Z}_2}{\partial R} = -\int \frac{\partial}{\partial R}\left(1 - e^{-\beta V(\mathbf{r};\mathbf{R})}\right) e^{\beta V(\mathbf{r};\mathbf{R})}\rho(\mathbf{r})\mathrm{d}\mathbf{r} \tag{7}$$

where $V(\mathbf{r};\mathbf{R})$ (corresponding to V_{bcc} in the main text; here we use shortened notation) is the potential landscape for a particle of species 2 due to the presence of the two particles of species 1 and $\rho(\mathbf{r})$ is the density of species 2 spheres.

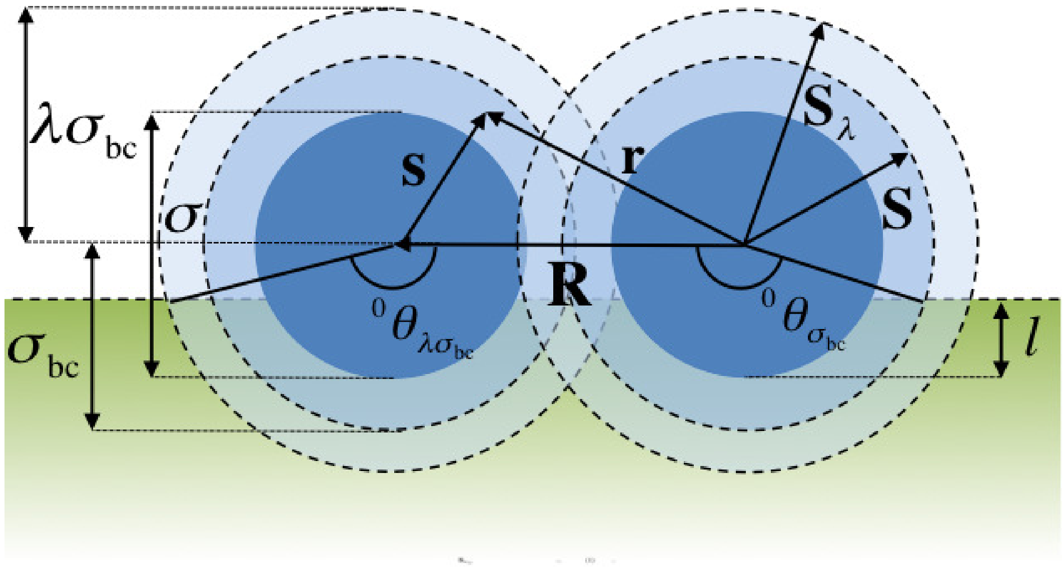

FIGURE 1. **Scheme of the geometry of the problem**

Using Supplementary equation 5, $V(\mathbf{r};\mathbf{R}) = V_{\rm bc}(|\mathbf{r}|) + V_{\rm bc}(|\mathbf{r}-\mathbf{R}|)$ can be written as:

$$V(\mathbf{r};\mathbf{R}) = \begin{cases} \infty & \text{if } r < \sigma_{\rm bc} \text{ or } |\mathbf{r}-\mathbf{R}| < \sigma_{\rm bc} \\ -\epsilon & \text{if } \sigma_{\rm bc} \le r < \lambda\sigma_{\rm bc} \text{ xor } \sigma_{\rm bc} \le |\mathbf{r}-\mathbf{R}| < \lambda\sigma_{\rm bc} \\ -2\epsilon & \text{if } \sigma_{\rm bc} \le r < \lambda\sigma_{\rm bc} \text{ and } \sigma_{\rm bc} \le |\mathbf{r}-\mathbf{R}| < \lambda\sigma_{\rm bc} \\ 0 & \text{if } r \ge \lambda\sigma_{\rm bc} \text{ and } |\mathbf{r}-\mathbf{R}| \ge \lambda\sigma_{\rm bc} \end{cases} \tag{8}$$

And the corresponding Meyer function can be encoded using the characteristic function

$$\mathscr{H}_D(\mathbf{r}) = \begin{cases} 1 & \text{if } |\mathbf{r}| < D \\ 0 & \text{if } |\mathbf{r}| \ge D \end{cases} \tag{9}$$

obtaining:

(10)

$$1 - e^{-\beta V(\mathbf{r};\mathbf{R})} =$$

$$\begin{aligned} &= \left(1 - e^{\beta\epsilon}\right)\left[\mathscr{H}_{\lambda\sigma_{\rm bc}}(\mathbf{r}) + \mathscr{H}_{\lambda\sigma_{\rm bc}}(\mathbf{r}-\mathbf{R})\right] + \\ &\left(2e^{\beta\epsilon} - e^{2\beta\epsilon} - 1\right)\mathscr{H}_{\lambda\sigma_{\rm bc}}(\mathbf{r})\mathscr{H}_{\lambda\sigma_{\rm bc}}(\mathbf{r}-\mathbf{R}) + \\ &\left(e^{2\beta\epsilon} - e^{\beta\epsilon}\right)\left[\mathscr{H}_{\sigma_{\rm bc}}(\mathbf{r})\mathscr{H}_{\lambda\sigma_{\rm bc}}(\mathbf{r}-\mathbf{R}) + \mathscr{H}_{\lambda\sigma_{\rm bc}}(\mathbf{r})\mathscr{H}_{\sigma_{\rm bc}}(\mathbf{r}-\mathbf{R})\right] - \\ &e^{2\beta\epsilon}\mathscr{H}_{\sigma_{\rm bc}}(\mathbf{r})\mathscr{H}_{\sigma_{\rm bc}}(\mathbf{r}-\mathbf{R}) + \\ &e^{\beta\epsilon}\left[\mathscr{H}_{\sigma_{\rm bc}}(\mathbf{r}) + \mathscr{H}_{\sigma_{\rm bc}}(\mathbf{r}-\mathbf{R})\right] \end{aligned}$$

Using Supplementary equations 6, 7 and 10 we can express:

$$
\begin{aligned}
&\frac{\partial \mathrm{Z}_2}{\partial R} = \\
&\quad -\left(1-e^{\beta\epsilon}\right)\int \frac{\mathbf{R}}{R}\cdot\frac{\mathbf{r}-\mathbf{R}}{|\mathbf{r}-\mathbf{R}|}\delta\left(|\mathbf{r}-\mathbf{R}|-\lambda\sigma_{\mathrm{bc}}\right)e^{-\beta V(\mathbf{r};\mathbf{R})}\rho(\mathbf{r})\mathrm{Z}_2\mathrm{d}\mathbf{r}- \\
&\quad \left(2e^{\beta\epsilon}-e^{2\beta\epsilon}-1\right)\int \frac{\mathbf{R}}{R}\cdot\frac{\mathbf{r}-\mathbf{R}}{|\mathbf{r}-\mathbf{R}|}\mathscr{H}_{\lambda\sigma_{\mathrm{bc}}}(\mathbf{r})\delta\left(|\mathbf{r}-\mathbf{R}|-\lambda\sigma_{\mathrm{bc}}\right)e^{-\beta V(\mathbf{r};\mathbf{R})}\rho(\mathbf{r})\mathrm{Z}_2\mathrm{d}\mathbf{r}- \\
&\quad \left(e^{2\beta\epsilon}-e^{\beta\epsilon}\right)\int \frac{\mathbf{R}}{R}\cdot\frac{\mathbf{r}-\mathbf{R}}{|\mathbf{r}-\mathbf{R}|}\mathscr{H}_{\sigma_{\mathrm{bc}}}(\mathbf{r})\delta\left(|\mathbf{r}-\mathbf{R}|-\lambda\sigma_{\mathrm{bc}}\right)e^{-\beta V(\mathbf{r};\mathbf{R})}\rho(\mathbf{r})\mathrm{Z}_2\mathrm{d}\mathbf{r}+ \\
&\quad \left(e^{2\beta\epsilon}-e^{\beta\epsilon}\right)\int \frac{\mathbf{R}}{R}\cdot\frac{\mathbf{r}-\mathbf{R}}{|\mathbf{r}-\mathbf{R}|}\mathscr{H}_{\lambda\sigma_{\mathrm{bc}}}(\mathbf{r})\delta\left(|\mathbf{r}-\mathbf{R}|-\sigma_{\mathrm{bc}}\right)e^{-\beta V(\mathbf{r};\mathbf{R})}\rho(\mathbf{r})\mathrm{Z}_2\mathrm{d}\mathbf{r} \\
&\quad e^{2\beta\epsilon}\int \frac{\mathbf{R}}{R}\cdot\frac{\mathbf{r}-\mathbf{R}}{|\mathbf{r}-\mathbf{R}|}\mathscr{H}_{\sigma_{\mathrm{bc}}}(\mathbf{r})\delta\left(|\mathbf{r}-\mathbf{R}|-\sigma_{\mathrm{bc}}\right)e^{-\beta V(\mathbf{r};\mathbf{R})}\rho(\mathbf{r})\mathrm{Z}_2\mathrm{d}\mathbf{r}+ \\
&\quad e^{\beta\epsilon}\int \frac{\mathbf{R}}{R}\cdot\frac{\mathbf{r}-\mathbf{R}}{|\mathbf{r}-\mathbf{R}|}\delta\left(|\mathbf{r}-\mathbf{R}|-\sigma_{\mathrm{bc}}\right)e^{-\beta V(\mathbf{r};\mathbf{R})}\rho(\mathbf{r})\mathrm{Z}_2\mathrm{d}\mathbf{r}
\end{aligned}
\tag{11}
$$

To solve the above integrals we first perform the change of variable $\mathbf{s} = \mathbf{r}-\mathbf{R}$, than introduce spherical coordinates with $\cos\theta = \mathbf{R}\cdot\mathbf{s}/Rs$.
The first and the sixt integrals can be solved analogously. The first gives:

$$
\begin{aligned}
&\int \frac{\mathbf{R}}{R}\cdot\frac{\mathbf{s}}{s}\delta\left(s-\lambda\sigma_{\mathrm{bc}}\right)e^{-\beta V(\mathbf{s}+\mathbf{R})}\rho\left(\mathbf{s}+\mathbf{R}\right)\mathrm{Z}_2 d\mathbf{s} = \\
&\qquad \int_0^\infty ds\int_0^\pi \mathrm{d}\theta\int_{-\pi}^{\pi}\mathrm{d}\phi\frac{\mathbf{R}}{R}\cdot\frac{\mathbf{s}}{s}\delta\left(s-\lambda\sigma_{\mathrm{bc}}\right)e^{\beta V(\mathbf{s}+\mathbf{R})}\times \\
&\qquad \rho(\mathbf{s}+\mathbf{R})\mathrm{Z}_2 s^2\sin\theta = \\
&\qquad \lambda\sigma_{\mathrm{bc}}^2\int_0^\pi \mathrm{d}\theta\int_{-\pi}^{\pi}\mathrm{d}\phi\cos\theta\sin\theta e^{\beta V(\mathbf{S}_\lambda)}\rho(\mathbf{S}_\lambda)\mathrm{Z}_2
\end{aligned}
\tag{12}
$$

The second and the fourth integrals are again similar. The fourth gives:

$$
\begin{aligned}
&\int \mathscr{H}_{\lambda\sigma_{\mathrm{bc}}}\frac{\mathbf{R}}{R}\cdot\frac{\mathbf{r}-\mathbf{R}}{|\mathrm{r}-\mathrm{R}|}\delta\left(|\mathbf{r}-\mathbf{R}|-\sigma_{\mathrm{bc}}\right)e^{\beta V(\mathbf{r};\mathbf{R})}\rho(\mathbf{r})\mathrm{Z}_2\mathrm{d}\mathbf{r} = \\
&\sigma_{\mathrm{bc}}^2\int_0^\pi \mathrm{d}\theta\int_{-\pi}^{\pi}d\phi\mathscr{H}_{\lambda\sigma_{\mathrm{bc}}}(\mathbf{S})\cos\theta\sin\theta e^{\beta V(\mathbf{S})}\rho(\mathbf{S})\mathrm{Z}_2
\end{aligned}
\tag{13}
$$

The third and the fifth integrals are identically zero.
The vectors $\mathbf{S}$ and $\mathbf{S}_\lambda$ with $|\mathbf{S}| = \sigma_{\mathrm{bc}}$ and $|\mathbf{S}_\lambda| = \lambda\sigma_{\mathrm{bc}}$ are shown in Supplementary Figure 1.
Following reference [4] we can account for the $\mathscr{H}$ functions by introducing

the densities:

$$
(14)\quad
\begin{aligned}
{}^1\rho(\mathbf{S}_\lambda) &= \begin{cases} \rho(\mathbf{S}_\lambda) & \text{if } 0 \le \theta <^1 \theta_{\lambda\sigma_{\rm bc}} \\ 0 & \text{otherwise} \end{cases} \\
{}^2\rho(\mathbf{S}_\lambda) &= \begin{cases} \rho(\mathbf{S}_\lambda) & \text{if } {}^1\theta_{\lambda\sigma_{\rm bc}} \le \theta <^2 \theta_{\lambda\sigma_{\rm bc}} \\ 0 & \text{otherwise} \end{cases} \\
{}^1\rho(\mathbf{S}) &= \begin{cases} \rho(\mathbf{S}) & \text{if } 0 \le \theta <^1 \theta_{\sigma_{\rm bc}} \\ 0 & \text{otherwise} \end{cases} \\
{}^2\rho(\mathbf{S}) &= \begin{cases} \rho(\mathbf{S}) & \text{if } {}^1\theta_{\sigma_{\rm bc}} \le \theta <^2 \theta_{\sigma_{\rm bc}} \\ 0 & \text{otherwise} \end{cases}
\end{aligned}
$$

where

$$
(15)\quad
\begin{aligned}
{}^1\theta_{\lambda\sigma_{\rm bc}} &= \arccos\left(\frac{R^2}{2\lambda\sigma_{\rm bc}R}\right) \\
{}^2\theta_{\lambda\sigma_{\rm bc}} &= \arccos\left(\frac{\lambda^2\sigma_{\rm bc}^2 - R^2 - \sigma_{\rm bc}^2}{-2\sigma_{\rm bc}R}\right) \\
{}^1\theta_{\sigma_{\rm bc}} &= \arccos\left(\frac{\sigma_{\rm bc}^2 - R^2 - \lambda\sigma_{\rm bc}^2}{-2\lambda\sigma_{\rm bc}R}\right) \\
{}^2\theta_{\sigma_{\rm bc}} &= \arccos\left(\frac{R^2}{2\sigma_{\rm bc}R}\right)
\end{aligned}
$$

From this point, our derivation differs from reference [4] because we need to take into account partial penetration of the colloid. In our case, $\rho(\mathbf{S})$ and $\rho(\mathbf{S}_\lambda)$ have no azimuthal symmetry so the integrations in ϕ are not trivial. As shown in Supplementary Figure 1, we define the angles:

$$
(16)\quad {}^0\theta_{\lambda\sigma_{\rm bc}} = \arccos\left(\frac{h}{\lambda\sigma_{\rm bc}}\right) + \frac{\pi}{2}
$$

$$
(17)\quad {}^0\theta_{\sigma_{\rm bc}} = \arccos\left(\frac{h}{\sigma_{\rm bc}}\right) + \frac{\pi}{2}
$$

and redefine the densities appearing in the integrals above as:

(18)

$$
\rho\left(\mathbf{S}_\lambda\right) = \begin{cases} {}^1\rho(\mathbf{S}_\lambda) +^2 \rho(\mathbf{S}_\lambda) & \text{if } \theta \le {}^0\theta_{\lambda\sigma_{\rm bc}} \text{ and } |\phi| \le \arcsin\left[\sqrt{1-\left(\frac{\sin^0\theta_{\lambda\sigma_{\rm bc}}}{\sin\theta}\right)^2}\right] \\ 0 & \text{otherwise} \end{cases}
$$

$$
\rho\left(\mathbf{S}\right) = \begin{cases} {}^1\rho(\mathbf{S}) +^2 \rho(\mathbf{S}) & \text{if } \theta \le {}^0\theta_{\sigma_{\rm bc}} \text{ and } |\phi| \le \arcsin\left[\sqrt{1-\left(\frac{\sin^0\theta_{\sigma_{\rm bc}}}{\sin\theta}\right)^2}\right] \\ 0 & \text{otherwise} \end{cases}
$$

$f(R)$ can be put in the form:

$$
\begin{aligned}
f(R) &= -\frac{1}{\beta}\sigma_{\mathrm{bc}}^2\left[I(R) + \lambda^2(1-e^{\beta\epsilon})I_\lambda(R)\right] \\
I(R) &= \int_0^\pi \mathrm{d}\theta \int_{-\pi}^{\pi} \mathrm{d}\phi\rho(\mathbf{S};R)\cos\theta\sin\theta \\
I_\lambda(R) &= \int_0^\pi \mathrm{d}\theta \int_{-\pi}^{\pi} \mathrm{d}\phi\rho(\mathbf{S}_\lambda;R)\cos\theta\sin\theta
\end{aligned} \tag{19}
$$

Finally, using Supplementary equations 14 and 18, the integrals $I(R)$ and $I_\lambda(R)$ can be expressed as:

$$
\begin{aligned}
I(R) &= \int_{\pi-{}^0\theta_{\sigma_{\mathrm{bc}}}}^{{}^0\theta_{\sigma_{\mathrm{bc}}}} \arcsin\left[\sqrt{1-\left(\frac{\sin^0\theta_{\sigma_{\mathrm{bc}}}}{\sin\theta}\right)^2}\right]\tilde{\rho}(\mathbf{S};R)\cos\theta\sin\theta\mathrm{d}\theta \\
I_\lambda(R) &= \int_{\pi-{}^0\theta_{\lambda\sigma_{\mathrm{bc}}}}^{{}^0\theta_{\lambda\sigma_{\mathrm{bc}}}} \arcsin\left[\sqrt{1-\left(\frac{\sin^0\theta_{\lambda\sigma_{\mathrm{bc}}}}{\sin\theta}\right)^2}\right]\tilde{\rho}(\mathbf{S}_\lambda;R)\cos\theta\sin\theta\mathrm{d}\theta
\end{aligned} \tag{20}
$$

where we renamed

$$
\begin{aligned}
\tilde{\rho}\left(\mathbf{S}_\lambda\right) &=^1 \rho(\mathbf{S}_\lambda) +^2 \rho(\mathbf{S}_\lambda) \\
\tilde{\rho}\left(\mathbf{S}\right) &=^1 \rho(\mathbf{S}) +^2 \rho(\mathbf{S})
\end{aligned} \tag{21}
$$

2.1. **Analytical expression for the force in the ideal gas approximation.** In the ideal gas approximation:

$$
\rho(\mathbf{r};R) = \rho e^{-\beta V(\mathbf{r};R)} \tag{22}
$$

We can use Supplementary equation 8 to compute $\tilde{\rho}(\mathbf{S})$ and $\tilde{\rho}(\mathbf{S}_\lambda)$:

$$
\begin{aligned}
\tilde{\rho}(\mathbf{S}_\lambda) &= \begin{cases} \rho & \text{if } 0 \le \theta <^1 \theta_{\lambda\sigma_{\mathrm{bc}}} \\ \rho e^{\beta\epsilon_{12}} & \text{if } {}^1\theta_{\lambda\sigma_{\mathrm{bc}}} \le \theta <^2 \theta_{\lambda\sigma_{\mathrm{bc}}} \\ 0 & \text{otherwise} \end{cases} \\
\tilde{\rho}(\mathbf{S}) &= \begin{cases} \rho e^{\beta\epsilon_{12}} & \text{if } 0 \le \theta <^1 \theta_{\sigma_{\mathrm{bc}}} \\ \rho e^{2\beta\epsilon_{12}} & \text{if } {}^1\theta_{\sigma_{\mathrm{bc}}} \le \theta <^2 \theta_{\sigma_{\mathrm{bc}}} \\ 0 & \text{otherwise} \end{cases}
\end{aligned} \tag{23}
$$

Integrations in Supplementary equation 20 can be solved analytically:

$$
\begin{aligned}
&\int \arcsin\left[\sqrt{1-\left(\frac{\sin^0\theta}{\sin\theta}\right)^2}\right]\cos\theta\sin\theta\mathrm{d}\theta = \\
&\frac{1}{2}\sin^0\theta\sin\theta\left[\frac{\sin\theta}{\sin^0\theta}\arccos\left(\frac{\sin^0\theta}{\sin\theta}\right) - \sqrt{1-\left(\frac{\sin^0\theta}{\sin\theta}\right)}\right] = \chi(\theta;^0\theta).
\end{aligned} \tag{24}
$$

We define the following set of threshold distances:

(25)

$$\begin{aligned}
\pi &=^1 \theta_{\lambda\sigma_{\rm bc}} \rightarrow R = R_1 = 2\sigma_{\rm bc} \\
\pi &=^2 \theta_{\lambda\sigma_{\rm bc}} =^1 \theta_{\sigma_{\rm bc}} \rightarrow R = R_2 = \sigma_{\rm bc} + \lambda\sigma_{\rm bc} \\
\pi &=^2 \theta_{\sigma_{\rm bc}} \rightarrow R = R_3 = 2\lambda\sigma_{\rm bc} \\
{}^0\theta_{\lambda\sigma_{\rm bc}} &=^1 \theta_{\lambda\sigma_{\rm bc}} \rightarrow R =^1 R^0_{\lambda\sigma_{\rm bc}} = -2\lambda\sigma_{\rm bc}\cos({}^0\theta_{\lambda\sigma_{\rm bc}}) \\
{}^0\theta_{\lambda\sigma_{\rm bc}} &=^2 \theta_{\lambda\sigma_{\rm bc}} \rightarrow R =^2 R^0_{\lambda\sigma_{\rm bc}} = -\sigma_{\rm bc}\cos\theta_0\left[1+\sqrt{1-\frac{1-\lambda^2}{\cos^2({}^0\theta_{\lambda\sigma_{\rm bc}})}}\right] \\
{}^0\theta_{\sigma_{\rm bc}} &=^1 \theta_{\sigma_{\rm bc}} \rightarrow R =^1 R^0_{\sigma_{\rm bc}} = -\lambda\sigma_{\rm bc}\cos\theta_0\left[1+\sqrt{1-\frac{\lambda^2-1}{\lambda^2\cos^2({}^0\theta_{\sigma_{\rm bc}})}}\right] \\
{}^0\theta_{\sigma_{\rm bc}} &=^2 \theta_{\sigma_{\rm bc}} \rightarrow R =^2 R^0_{\sigma_{\rm bc}} = -2\sigma_{\rm bc}\cos({}^0\theta_{\sigma_{\rm bc}})
\end{aligned}$$

Using Supplementary equations 23 and 24, $I(R)$ and $I_\lambda(R)$ can be calculated in a piece-wise fashion:

(26)

for $R_1 < R \leq R_2$ and $R \leq^2 R^0_{\sigma_{\rm bc}}$

$$I(R) = \rho e^{\beta\epsilon_{12}}\left[\left(1-e^{\beta\epsilon_{12}}\right)\chi({}^1\theta_{\sigma_{\rm bc}};{}^0\theta_{\sigma_{\rm bc}}) + e^{\beta\epsilon_{12}}\chi({}^2\theta_{\sigma_{\rm bc}};{}^0\theta_{\sigma_{\rm bc}}) - \chi\left(\pi -{}^0\theta_{\sigma_{\rm bc}};{}^0\theta_{\sigma_{\rm bc}}\right)\right]$$

for $(R_1 < R \leq R_2$ and ${}^2R^0_{\sigma_{\rm bc}} < R \leq^1 R^0_{\sigma_{\rm bc}})$ or $(R_2 < R \leq R_3$ and $R \leq^1 R^0_{\sigma_{\rm bc}})$

$$I(R) = \rho e^{\beta\epsilon_{12}}\left(1-e^{\beta\epsilon_{12}}\right)\left[\chi({}^1\theta_{\sigma_{\rm bc}};{}^0\theta_{\sigma_{\rm bc}}) - \chi\left(\pi -{}^0\theta_{\sigma_{\rm bc}};{}^0\theta_{\sigma_{\rm bc}}\right)\right]$$

for $(\sigma < R \leq R_1)$ or $(R_1 < R \leq R_2$ and $R >^1 R^0_{\sigma_{\rm bc}})$ or $(R > R_2)$

$$I(R) = 0$$

(27)

for $\sigma < R \leq R_2$ and $R \leq^2 R^0_{\lambda\sigma_{\rm bc}}$

$$I_\lambda(R) = \rho\left[\left(1-e^{\beta\epsilon_{12}}\right)\chi({}^1\theta_{\lambda\sigma_{\rm bc}};\theta_{\lambda\sigma_{\rm bc}}) + e^{\beta\epsilon_{12}}\chi({}^2\theta_{\lambda\sigma_{\rm bc}};\theta_{\lambda\sigma_{\rm bc}}) - \chi\left(\pi - \theta_{\lambda\sigma_{\rm bc}};\theta_{\lambda\sigma_{\rm bc}}\right)\right]$$

for $(\sigma < R \leq R_2$ and ${}^2R^0_{\lambda\sigma_{\rm bc}} < R \leq^1 R^0_{\lambda\sigma_{\rm bc}})$ or $(R_2 < R \leq R_3$ and $R \leq^2 R^0_{\lambda\sigma_{\rm bc}})$

$$I_\lambda(R) = \rho\left(1-e^{\beta\epsilon_{12}}\right)\left[\chi({}^1\theta_{\lambda\sigma_{\rm bc}};\theta_{\lambda\sigma_{\rm bc}}) - \chi({}^2\theta_{\lambda\sigma_{\rm bc}};\theta_{\lambda\sigma_{\rm bc}})\theta\right]$$

for $(\sigma < R \leq R_2$ and $R >^1 R^0_{\lambda\sigma_{\rm bc}})$ or $(R_2 < R \leq R_3$ and $R >^2 R^0_{\lambda\sigma_{\rm bc}})$ or $(R > R_3)$

$$I_\lambda(R) = 0$$

2.2. **Analytical expression for the force using correction for blob-blob repulsion.** We substitute Supplementary equation 22 with Supplementary equation 39, derived in the following section. To modify the colloid-colloid force we need replace Supplementary equation 23 with:

(28)
$$\tilde{\rho}(\mathbf{S}_\lambda) = \begin{cases} \rho_0 & \text{if } 0 \leq \theta <^1 \theta_{\lambda\sigma_{\rm bc}} \\ \rho_1 & \text{if } {}^1\theta_{\lambda\sigma_{\rm bc}} \leq \theta <^2 \theta_{\lambda\sigma_{\rm bc}} \\ 0 & \text{otherwise} \end{cases}$$
$$\tilde{\rho}(\mathbf{S}) = \begin{cases} \rho_1 & 0 \leq \theta <^1 \theta_{\sigma_{\rm bc}} \\ \rho_2 & \text{if } {}^1\theta_{\sigma_{\rm bc}} \leq \theta <^2 \theta_{\sigma_{\rm bc}} \\ 0 & \text{otherwise} \end{cases}$$

where

(29)
$$\rho_1 = \frac{\rho_0 e^{\beta\epsilon_{12}}}{1 + v\rho_0 e^{\beta\epsilon_{12}}}$$
$$\rho_2 = \frac{\rho_0 e^{2\beta\epsilon_{12}}}{1 + v\rho_0 e^{2\beta\epsilon_{12}}}$$

The integrals $I_\lambda(R)$ and $I(R)$ have now the form:

(30)
for $R_1 < R \leq R_2$ and $R \leq^2 R^0_{\sigma_{\rm bc}}$
$$I(R) = (\rho_1 - \rho_2)\,\chi({}^1\theta_{\sigma_{\rm bc}};{}^0\theta_{\sigma_{\rm bc}}) + \rho_2\chi({}^2\theta_{\sigma_{\rm bc}};{}^0\theta_{\sigma_{\rm bc}}) - \rho_1\chi\left(\pi -^0 \theta_{\sigma_{\rm bc}};{}^0\theta_{\sigma_{\rm bc}}\right)$$
for $(R_1 < R \leq R_2$ and ${}^2R^0_{\sigma_{\rm bc}} < R \leq^1 R^0_{\sigma_{\rm bc}})$ or $(R_2 < R \leq R_3$ and $R \leq^1 R^0_{\sigma_{\rm bc}})$
$$I(R) = (\rho_1 - \rho_2)\left[\chi({}^1\theta_{\sigma_{\rm bc}};{}^0\theta_{\sigma_{\rm bc}}) - \chi\left(\pi -^0 \theta_{\sigma_{\rm bc}};{}^0\theta_{\sigma_{\rm bc}}\right)\right]$$
for $(\sigma < R \leq R_1)$ or $(R_1 < R \leq R_2$ and $R >^1 R^0_{\sigma_{\rm bc}})$ or $(R > R_2)$
$$I(R) = 0$$

(31)
for $\sigma < R \leq R_2$ and $R \leq^2 R^0_{\lambda\sigma_{\rm bc}}$
$$I_\lambda(R) = (\rho_0 - \rho_1)\,\chi({}^1\theta_{\lambda\sigma_{\rm bc}};\theta_{\lambda\sigma_{\rm bc}}) + \rho_1\chi({}^2\theta_{\lambda\sigma_{\rm bc}};\theta_{\lambda\sigma_{\rm bc}}) - \rho_0\chi\left(\pi - \theta_{\lambda\sigma_{\rm bc}};\theta_{\lambda\sigma_{\rm bc}}\right)$$
for $(\sigma < R \leq R_2$ and ${}^2R^0_{\lambda\sigma_{\rm bc}} < R \leq^1 R^0_{\lambda\sigma_{\rm bc}})$ or $(R_2 < R \leq R_3$ and $R \leq^2 R^0_{\lambda\sigma_{\rm bc}})$
$$I_\lambda(R)\,(\rho_0 - \rho_1)\left[\chi({}^1\theta_{\lambda\sigma_{\rm bc}};\theta_{\lambda\sigma_{\rm bc}}) - \chi({}^2\theta_{\lambda\sigma_{\rm bc}};\theta_{\lambda\sigma_{\rm bc}})\theta\right]$$
for $(\sigma < R \leq R_2$ and $R >^1 R^0_{\lambda\sigma_{\rm bc}})$ or $(R_2 < R \leq R_3$ and $R >^2 R^0_{\lambda\sigma_{\rm bc}})$ or $(R > R_3)$
$$I_\lambda(R) = 0$$

3. Derivation of the real-gas density distribution of blobs

The osmotic pressure $\Pi(\rho(\mathbf{r}))$ of Brownian spheres is related to the external force field $\mathbf{F}(\mathbf{r})$ by the relation [5]:

$$\mathbf{F}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})}\nabla_r \Pi(\rho(\mathbf{r})) \tag{32}$$

In the first order expansion in terms of density, the osmotic pressure is given by [5]:

$$\frac{d\Pi}{d\rho} = \frac{1}{\beta}(1 + v\rho). \tag{33}$$

Integrating we get:

$$\Pi(\rho) = \frac{1}{\beta}\left(\rho + \frac{1}{2}v\rho^2\right) + A \tag{34}$$

Where v is the volume of the spheres and A is a constant.
Substituting Supplementary equation 34 in Supplementary equation 32 we have:

$$\begin{aligned}\mathbf{F} = -\nabla_r V =& \frac{1}{\beta}\frac{1}{\rho}(v\rho\nabla_r\rho + \nabla\rho) = \\ & \frac{1}{\beta}\nabla_r(v\rho + \log\rho).\end{aligned} \tag{35}$$

Integrating:

$$-V = \frac{1}{\beta}(v\rho + \log\rho) + B. \tag{36}$$

Which gives:

$$\rho = Ce^{-\beta V}e^{-v\rho} \tag{37}$$

In the limit $v\rho \ll 1$ we can expand the exponential at the right hand side:

$$\begin{aligned}\rho =& Ce^{-\beta V}(1 - v\rho) \rightarrow \\ \rho =& \frac{Ce^{-\beta V}}{1 + Cve^{-\beta V}}\end{aligned} \tag{38}$$

In the limit of ideal gas (i.e. $v = 0$) we should recover Supplementary equation 22, thus $C = \rho_0$.
The final result is then:

$$\rho(\mathbf{r};\mathbf{R}) = \frac{\rho_0 e^{-\beta V(\mathbf{r};\mathbf{R})}}{1 + \rho_0 v e^{-\beta V(\mathbf{r};\mathbf{R})}} \tag{39}$$

The reader should note that the osmotic pressure defined here does not correspond to the monomer osmotic pressure. In fact, the osmotic pressure of monomers in a self avoid random walk (SAWR, describing a swollen polymer chain in good solvent) would not follow a quadratic dependence on the monomer density but a power law with fractional exponent [6]. However, we have already made use of correct scaling laws of SAWRs when defining the size and the amplitude of blob–blob repulsion. Once the polymer–network has been mapped onto a network of blobs, they can be treated as generic Brownian particles.

4. Repulsive regimes in the potential of mean force

Our theory recovers regimes of net repulsion in the polymer–network mediated potential of mean force between colloidal particles. In general, this occurs when the density of the polymer coronae surrounding the colloids is high–enough that the disjoining osmotic pressure or steric repulsion between them prevents their overlap, and therefore the formation of the bridge. A way to reach this regime consists in simply increasing the blob density ρ. As demonstrated in Supplementary Figure 2, upon increasing ρ, we first see a short–range repulsion coexisting with a slightly longer range attraction. Then the potential becomes fully repulsive and strong enough to prevent the colloids to come in direct contact.
Analogous effect can be obtained by slightly increasing δ, and consequently the blob–colloid attraction which ultimately causes an increased blob density in the corona surrounding the colloids.
Also, changing the scaling behavior of the chains, for example to account for solvents of different quality, can give rise to net repulsive regimes. Indeed, if the ideal chain scaling is used, one needs to redefine the blob dimension $R_{\mathrm{F}} = bN^{1/2}$, as well as the range and the depth of the blob–colloid interaction $\xi_{\mathrm{ads}} = b/\delta$ and $\epsilon_{\mathrm{ads}} = -k_{\mathrm{B}}NT\delta^2$. ϵ_{ads} turns out to be significantly bigger compared with what calculated for SARW (10 $k_{\mathrm{B}}T$ for $b = 0.005$ $N = 1000$ and $\delta = 0.1$ compared with 3 $k_{\mathrm{B}}T$). This leads to a purely repulsive potential of mean force due to the saturation of the surface of the colloids.

5. Monte Carlo simulations

5.1. **Summary of the model.** The polymer gel is modeled as a network of M blobs. The overall energy of the network is given by

$$U_{\mathrm{network}}(\{\mathbf{r}\}) = \sum_{i=1}^{M}\sum_{j=i+1}^{M}\left[V_{\mathrm{bb}}(r_{ij}) + C_{ij}V_{\mathrm{sp}}(r_{ij})\right] \tag{40}$$

where

$$C_{ij} = \begin{cases} 1 & \text{for nearest neighbors} \\ 0 & \text{otherwise.} \end{cases} \tag{41}$$

while $V_{\mathrm{bb}}(r)$ and $V_{\mathrm{sp}}(r)$ are reported in equations [1] and [2] of the main text. With $\{\mathbf{r}\}$ we indicate the set of blobs coordinates.

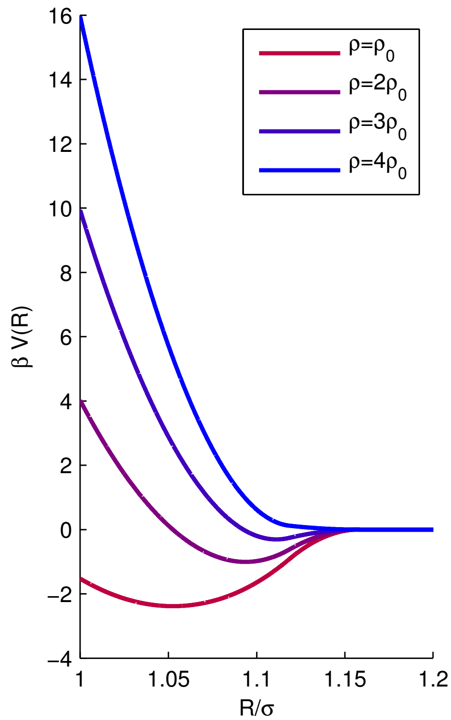

FIGURE 2. **Analytical potential of potential of mean force between two colloids fully embedded in the network at increasing values of blobs density**. $b = 0.005$, $\delta = 0.1$, $N = 1000$, $\rho_0 = 25/\sigma^3$.

M_c colloids of diameter σ interact one to each other with hard sphere potential

$$V_{\rm hs}(R) = \begin{cases} +\infty & \text{if } R < \sigma \\ 0 & \text{if } R > \sigma \end{cases} \tag{42}$$

The colloids also interact with the blobs with energy $V_{\rm bc}(r)$ (Supplementary equation 5) . Finally, a gravity force $\mathbf{F} = -F\hat{z}$ is acting on the colloids. The overall energy of the colloids is thus:

(43)

$$U_{\rm colloids}(\{\mathbf{R}\},\{\mathbf{r}\}) = \sum_{I=1}^{M_c}\left[\sum_{J=I+1}^{M_c} V_{\rm hs}(R_{IJ}) + \sum_{j=1}^{M} V_{\rm bc}(|\mathbf{R}_I - \mathbf{r}_j|) - FZ_I\right]$$

where with $\{\mathbf{R}\}$ we indicated the set of colloids coordinates.
The total energy of the system to be used in the simulations is:

$$U(\{\mathbf{R}\},\{\mathbf{r}\}) = U_{\rm network}(\{\mathbf{r}\}) + U_{\rm colloids}(\{\mathbf{R}\},\{\mathbf{r}\}). \tag{44}$$

5.2. **Details of the simulations.** We simulated the system within the NVT ensemble using the Metropolis Monte Carlo algorithm. Periodic boundary conditions were used in the directions x and y parallel to the network substrate with periodicity L. No periodic boundary conditions where used in the direction z normal to the network substrate. Blobs were initially arranged in a cubic lattice with cell parameter R_{F}. Consequently, the coordination of blobs in the bulk of the network was 6 while coordination of those at the upper and lower interface was 5. The bottom layer of blobs was confined around the plane $z = 0$ by the potential $V(z) = k_{\mathrm{B}}T(r/R_{\mathrm{F}})^{5/2}$ to avoid the folding of the network, but, at the same time allowing some flexibility in to mimic a thicker substrate.
The thickness of the network in the z direction was of 6 of layers of blobs. The number of blobs in the directions x and y was chosen in order to have a box size $L > 5\sigma$.
For single colloid simulations, used to evaluate colloid penetration l and bulk density of the network ρ_0, the colloid was allowed to fluctuate in all the directions. The distribution of the blobs was sampled using a 3D grid of mesh size 0.05σ moving with the reference frame of the colloid.
For two-colloids simulations, used to measure the pair potentials, MC moves were performed changing the distance R between the colloids and their height z. Using an Umbrella Sampling technique, the range of R was divided into widows of width 0.1σ with an overlap between adjacent windows of 0.05σ. R was sampled within each window and a histogram $H(R)$ for the whole range of distances was reconstructed using the Self-Consistent Histogram Method [7]. The pair potentials were then computed as $V(R) = -k_{\mathrm{B}}T \log H(R)$. To sample the distribution of blobs, the two colloids were held at fixed distance R but still allowed to fluctuate in z. The sampling was performed using the same grid as for the case of single colloid.
We define a MC cycle as a number of attempted moves (steps) equal to $M + M_{\mathrm{coll}}$ where M is the number of blobs and M_{coll} is a tunable integer. At every step, the probability of attempting to move a blob was $M/(M + M_{\mathrm{coll}})$ whears the probability of attempting to move a colloid was $M_{\mathrm{coll}}/(M+M_{\mathrm{coll}})$. We tuned M_{coll} in order to reach an optimal ratio between colloid and blob moves. The sampling frequency was once every 500 MC cycles. In Supplementary Table 1 we report details about simulations used to compute the curves in Figure 3 of the main body of the paper.

References

[1] Israelachvili J N (2011) *Intermolecular and surface forces: revised third edition* (Academic Press)
[2] Leikin S, Parsegian V A, Rau D C (1993) Hydration Forces. *Annu Rev Phys Chem* 44:339
[3] Attard P, (1989) Spherically inhomogeneous fluids. ii. hard-spheres solute in hard sphere solvent. *J Chem Phys* 91:3083-3089
[4] Fiocco D, Pastore G, Foffi G (2010) Effective forces in square well and square shoulder fluids. *J Phys Chem B* 114:12085-12095

TABLE 1. **Details about simulations used to compute colloid-colloid pair potentials showed in Figure 3 of the main text**. N is the number of monomers per blob, as described in the main body of the paper. M is the number of blobs in the simulation. The number of colloids is 2. To obtain the total number of Monte Carlo steps used to equilibrate the systems or sample the pair-potential, the number of cycles must be multiplied by the number of steps per cycle, in this case $M + 10$.

N	M	Equilibration Cycles ($\times 10^6$)	Production Cycles ($\times 10^8$)
700	2400	8.5	≈ 1.4
800	1944	8.5	≈ 1.7
900	1734	8.5	≈ 2.2
1000	1536	8.5	≈ 4.3

[5] Dhont J K G (1996) *An introduction to dynamics of colloids* (Elsevier)
[6] de Gennes P G (1979) Scaling concepts in polymer physics *Cornell University Press*
[7] Frenkel D, Smit B (1996) *Understanding Molecular Simulations* (Academic Press)