Supporting Information: Microscopic Theory of Self Assembly by Solvent Evaporation

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Rigorous definition of the droplet radii

We consider a system of N_t fluid (liquid+interface+gas) molecules and following the Gibbs convention, the volume of the interface is defined to be zero

$$V = V_{liquid} + V_{gas} \ . \tag{S1}$$

The number of solvent at the interface, the solvent excess number of particles, is defined to be

$$N_{interface} = N_t - (N_{liquid} + \ N_{gas}) = 0 \tag{S2}$$

which combined with Eq. S1 gives

$$N_t = n_{liquid} V_{liquid} + n_{gas} V_{gas} = \left(n_{liquid} - n_{gas}\right) V_{liquid} + n_{gas} V \tag{S3}$$

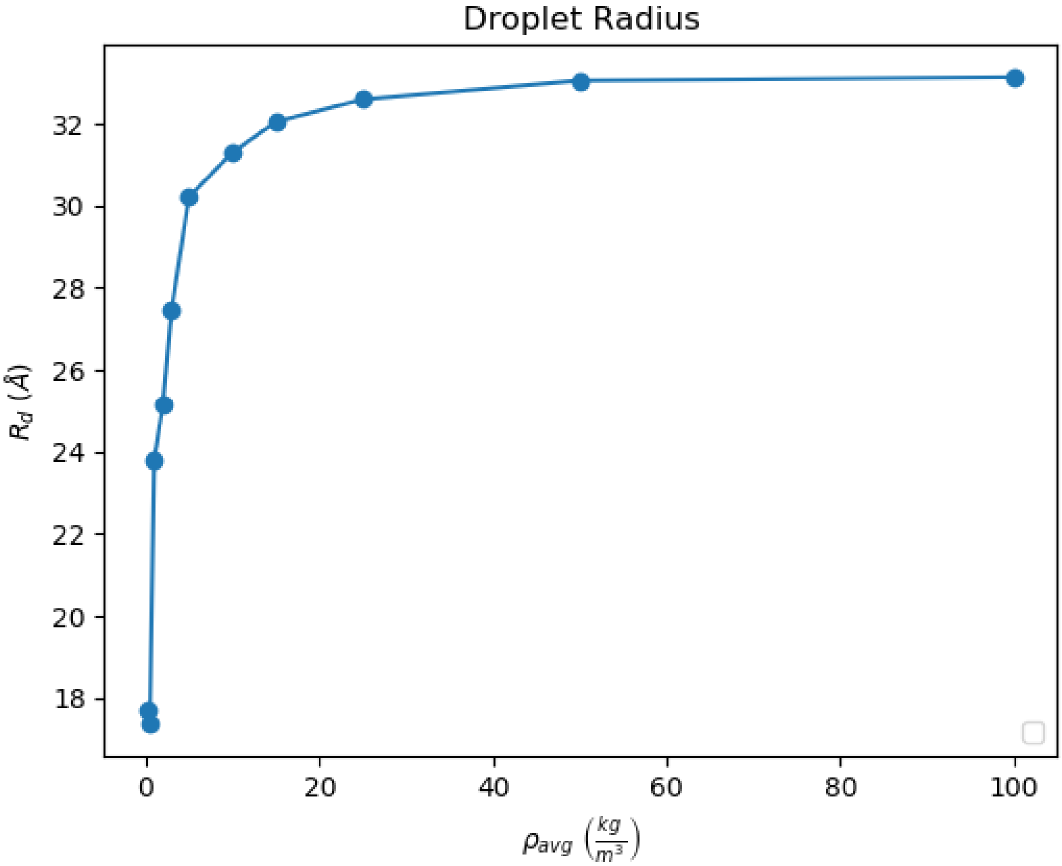


Figure S1: Curve of the droplet radius R_d defined by the Gibbs convention. For small values of R_d an additional convention is discussed.

where n_{liquid} and n_{gas} are respectively the bulk liquid and gas number densities. Then, the radius of the liquid droplet is defined as

$$R_d = \left(\frac{3V_{liquid}}{4\pi} \right)^{1/3} \quad . \tag{S4}$$

Applying Eq. S4 produces the plot in Fig. S1 for $N = 0$. The radius does not tend to 0 as it should, so instead we use the definition of the droplet radius given in the main paper (which does tend to 0) and scale the curve produced by that method to produce the same radius as Fig. S1 when the NCs are solvated. The scaling factor is the radius ratio $33/40 = .825$

Additional Results for Pure Toluene

The first relevant quantity is the equation of state (eos) of pure toluene as predicted by the simulation, which is necessary to obtain the free energy. As shown in Fig. S2, such eos is difficult to obtain from a direct simulation; In a typical simulation, setting the pressure at a value of order of 1 atm results in fluctuation that are ~ 50 atm. This difficulty arises because all thermostats have a small temperature fluctuation: From the thermodynamic relation

$$\left(\frac{\partial P}{\partial \rho} \right)_{T,N} = \frac{1}{\rho \kappa_T} \ , \tag{S5}$$

where κ_T is the isothermal compressibility, it follows approximately

$$P - P_r = \frac{1}{\kappa_T} \log(\rho/\rho_r) \ , \tag{S6}$$

assuming that κ_T is constant.

Fluctuations in volume are described by

$$\Delta V = \beta V \Delta T - \kappa_T V \Delta P \ . \tag{S7}$$

In the NVT ensemble, $\Delta V = 0$, hence, we derive the relation

$$\Delta P = \frac{\beta}{\kappa} \Delta T \ , \tag{S8}$$

which shows that small fluctuations (ΔT) in T immediately translate into fluctuations (ΔP) in P. For Toluene, for example, at 1 bar and $T = 380$ K, it is $\beta/\kappa = 7.5$ bar/K[34], and therefore $\Delta P = 7.5 \Delta T$. Simulation data illustrating this effect and showing its consistency with Eq. S7 and Eq. S8 is shown in Fig. S2 (right). Generally, with fluctuations of the order of $\Delta T \approx 1$ result in pressure fluctuations of a few tens of atmospheres. Long simulations are required to minimize those temperature fluctuations.

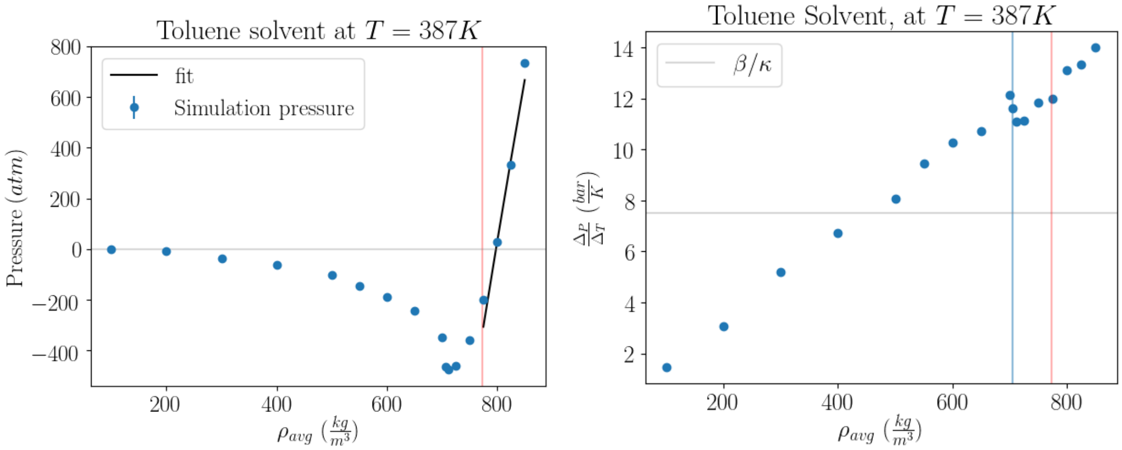


Figure S2: (Left) Simulation pressure as a function of ρ_{avg}. The red line indicates the experimental liquid density of toluene at $T = 387K$. The black curve is a fit from Eq. S6, yielding a value of $\kappa_T = 9.5(9) \times 10^{-5}$ atm^{-1}. (Right) Plot of the ratio between fluctuations in pressure ΔP and fluctuations in temperature ΔT, as a function of ρ_{avg}. The grey line is the experimental ratio β/κ, mentioned above, and the blue line is where simulations begin to show only a single liquid phase.

In Fig. S3 we show the density distribution at different values of ρ_{avg}. The two peak structure obtained for low ρ_{avg} reflects the two phase coexistence, see for example, Fig. 1. The saturated liquid density, as obtained from the simulation is given at $\rho_l^s = 780(4) \frac{kg}{m^3}$, which compares very well with the experimental result $\rho_l = 777.9$ kg/m^3, quoted above.

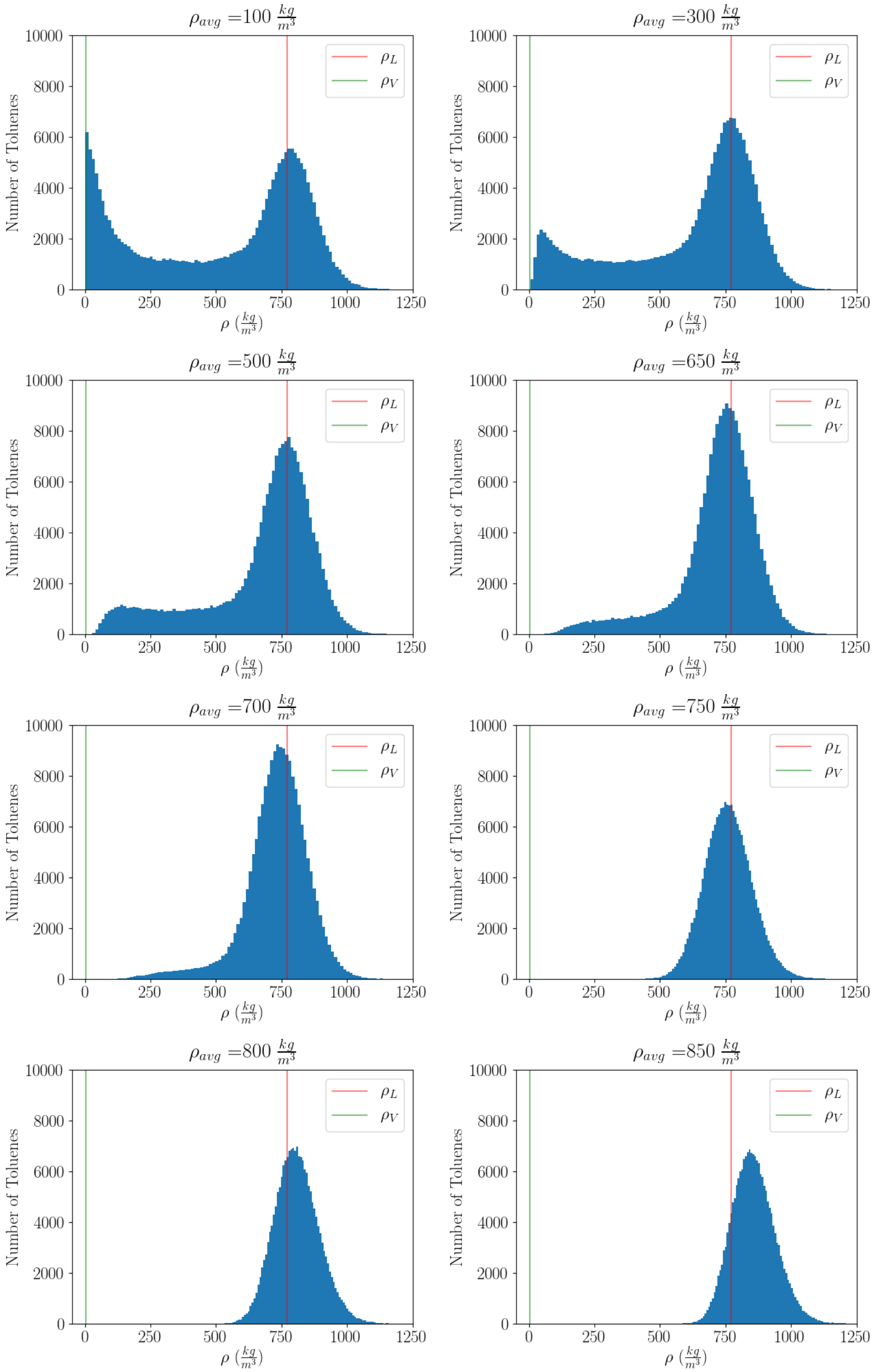


Figure S3: Histograms of local density, using the Voronoi construction and accumulated over 245 frames of the simulation, within the simulation box. Shown in the figures are the experimental liquid ($\rho_L = 777.9\ \frac{kg}{m^3}$) and vapor ($\rho_V = 3.3\ \frac{kg}{m^3}$) densities of toluene at $387K$, taken from Ref.[?]

Dependence of droplet radius R_d as a function of ρ_{avg}.

The derivation of the droplet radius R_d is the statement that all solvent molecules are either liquid or gas, see Eq. S1. Therefore, assuming that the NC is entirely contained within the liquid phase

$$\rho_g \left(V - \frac{4\pi}{3} R_d^3 \right) + \rho_l \left(\frac{4\pi}{3} R_d^3 - \frac{4\pi}{3} R_{HS}^3 N \right) = N_t M_w \ , \tag{S9}$$

where $R_{HS} = R_c \tau$ is the NC hard sphere radius, defined in Eq. 3. Therefore, it is

$$\frac{4\pi}{3} (\rho_l - \rho_g) R_d^3 = N_t \left(M_w + \frac{4\pi}{3} \rho_l R_{HS}^3 \frac{N}{N_t} - \rho_g \frac{V}{N_t} \right) \ , \tag{S10}$$

which, noting that $\rho_{avg} = M_w \frac{N_t}{V}$ leads to Eq. 7.

This assumption is generally correct, however, there is a small volume of ligand chains which exist outside the liquid phase, see Fig. S4, because the NCs prefer to stay near the interface between the liquid and gas phases. Because of this effect, the theoretical calculations tend to slightly overestimate the droplet radius because they include these chains in the total volume of the droplet. This effect is present in every configuration of NCs but becomes more pronounced with increasing N.

Complementary Results in NC self-assembly

Snapshots of the simulation as solvent evaporation occurs:

Dependence of the Nearest Neighbor distance on the droplet packing fraction η_{HS}

The results shown in Fig. S9 demonstrate the nearest neighbor distance as a function of the hard sphere packing fraction, defined in Eq. 4.

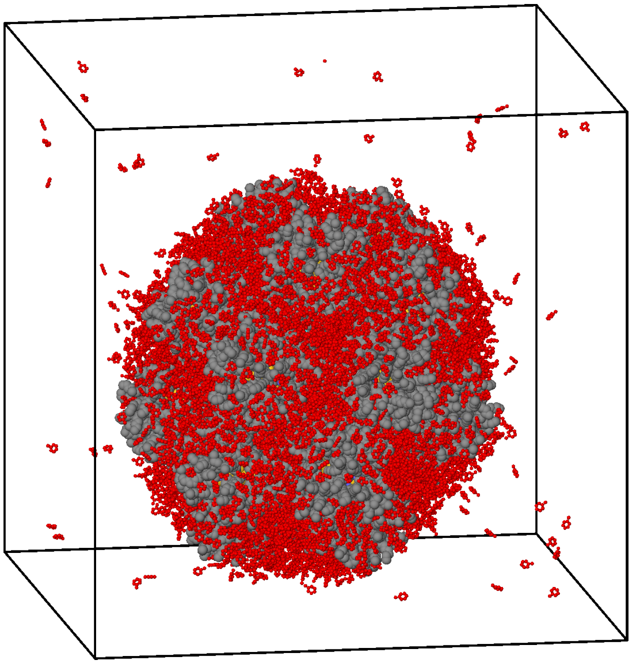


Figure S4: Illustration of the NC chains which exist outside of the droplet for $\rho_{avg} = 100\frac{kg}{m^3}$ on the $N = 21$ system. The gray chains are still visible in the image because they exist outside the droplet formed by the toluene molecules, which are colored red.

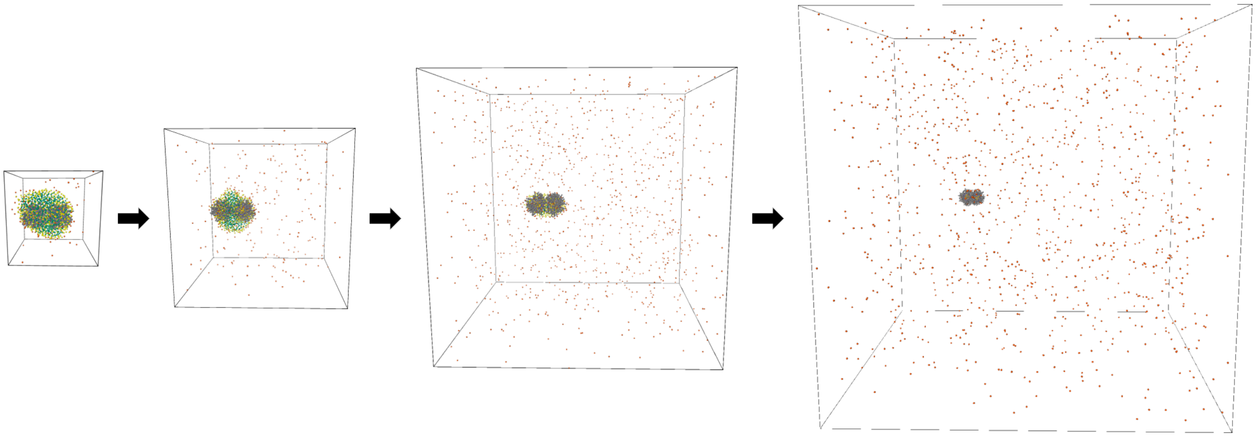


Figure S5: SE for N=2: As discussed, it follows the same steps as in Fig. 3.

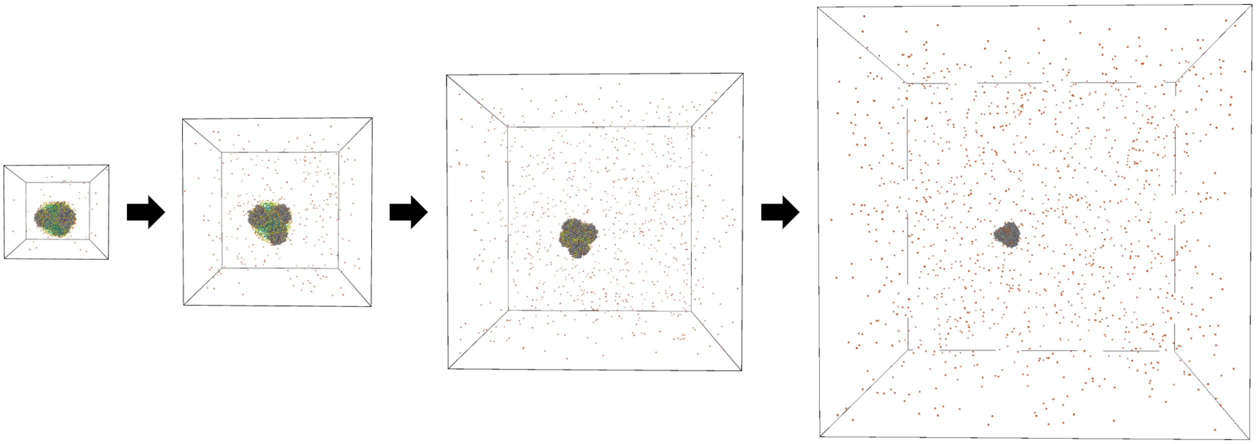


Figure S6: SE for N=4: As discussed, it follows the same steps as in Fig. 3.

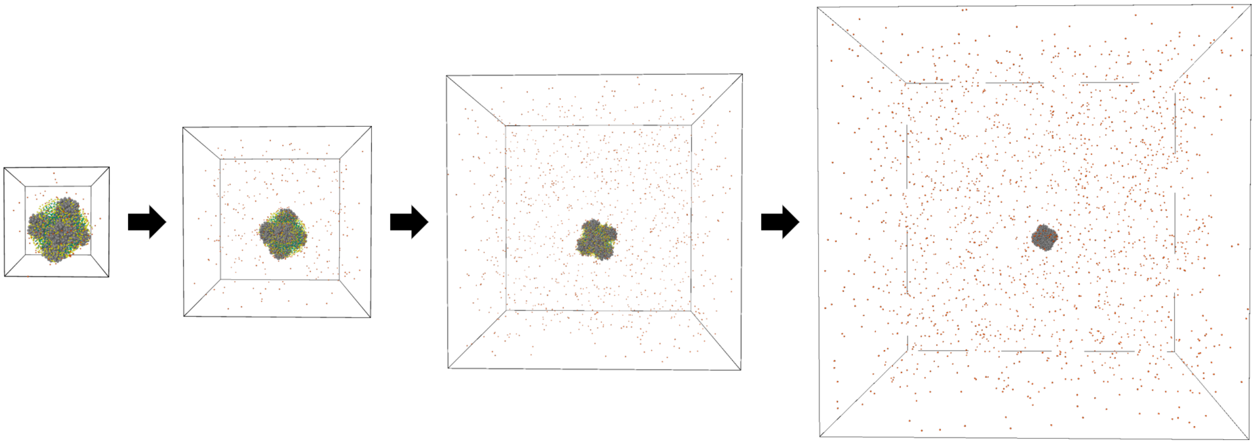


Figure S7: SE for N=6: As discussed, it follows the same steps as in Fig. 3.

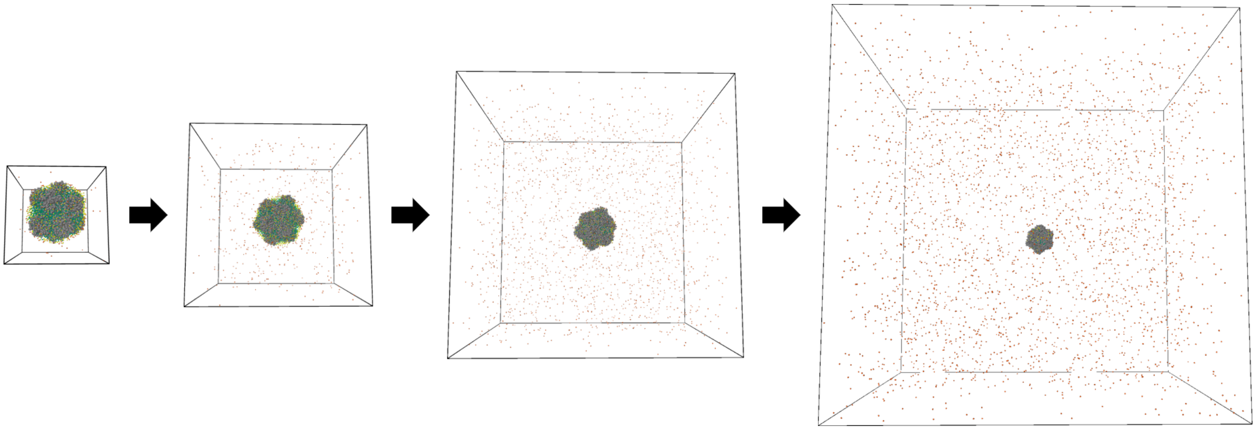


Figure S8: SE for N=13: As discussed, it follows the same steps as in Fig. 3.

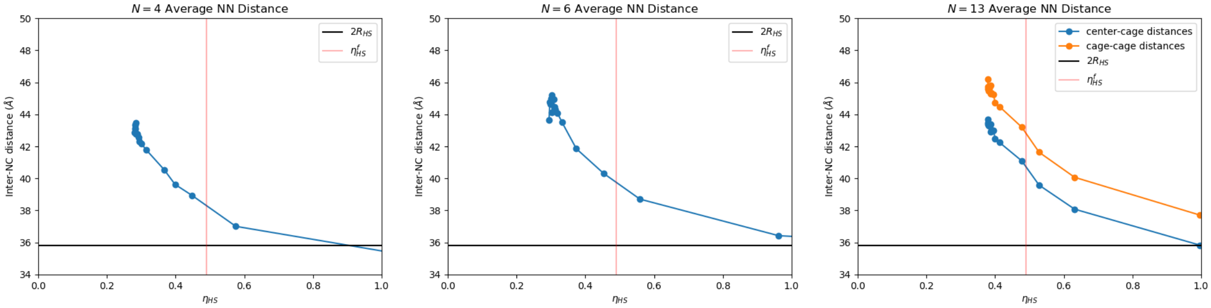


Figure S9: Average inter-NC distances shown as a function of η_{HS}.

Complementary results for the Free Energy

The free energy is obtained by integrating the pressure vs volume. If we define $V = l^3$, the free energy F_s change in expanding the system is given by

$$F_s(T, \rho_{avg}, l) - F_s(T, \rho_{avg0}, l_0) = -\int_{V_{initial}}^{V_{final}} P(V)dV = -\int_{l_0}^{l} 3l'^2 P(l')dl'. \tag{S11}$$

Note that the number of toluene molecules $N_t = \rho_{avg}V/M_w$ remains constant, and $V_{final} = l^3, V_{initial} = l_0^3$. We use the trapezoidal approximation to do the integral, so that the above expression becomes

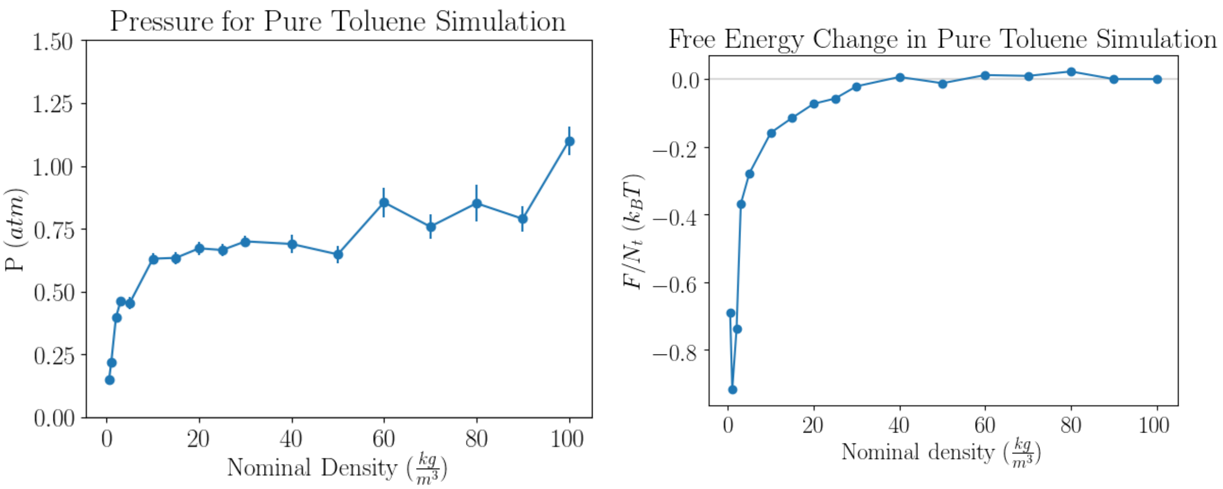
$$F_s(l_f) - F_s(l_0) = -\sum_{i=1}^{f}(l_i - l_{i-1})\frac{3l_i^2 P(l_i) + 3l_{i-1}^2 P(l_{i-1})}{2}. \tag{S12}$$

This calculated free energy is shown in Fig. S10. If the system consists of pure solvent only, after the droplet has completely evaporated the free energy is that of an ideal gas

$$F_s^g(l) \equiv F_{id}(P(l), T, N_t) = -N_t RT\left[\log\left(\frac{eP(l)}{RT\lambda_T^3}\right) + f_{int}(T)\right] , \tag{S13}$$

where $f_{int}(T)$ parameterizes the internal degrees of freedom and $\lambda_T = \left(\frac{2\pi\hbar^2}{mRT}\right)^{1/2}$ is the thermal wavelength. If some liquid remains, then the free energy of the liquid and the interface is obtained by subtracting the actual free energy to the ideal gas Eq. S13.

In Fig. S11 we show the eos as a function of ρ_{avg} and in Fig. S12 the calculated free



(a)

(b)

Figure S10: (Left) Pressure data for pure toluene, using the peaks of the distributions similar to Fig. 1b and then applying Eq. 5, as a function of nominal density. (Right) Calculated free energy change (from Eq. S12) per solvent molecule throughout the simulation.

energy. Note that after the solvent is completely evaporated, the free energy is, to a very good approximation (as the weak VdW NC toluene gas free energy is very small) given by

$$F_s(T, \rho_{av}, l; N) = F_{dry}(N) + F_{id}(T, P(l), N_t) = F_{pair} + F_s^g(l) \ , \tag{S14}$$

where F_{dry} is the value of the free energy for a dry sample at equilibrium, whose values are available from Ref.[37], and F_{id} is the free energy of an ideal gas of N particles contained in a volume $V = l^3$, see Eq. S13.

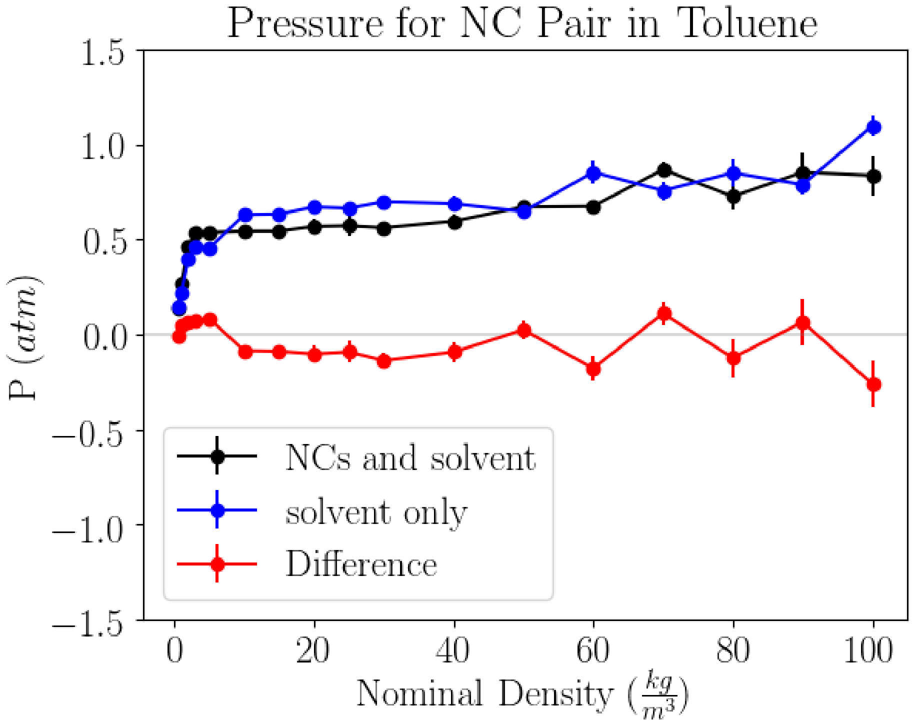


Figure S11: Pressure taken directly from the simulations for a pair of NCs in solvent (black), just solvent (blue), and the difference between the two (red). Error bars quoted are for a one standard deviation error.

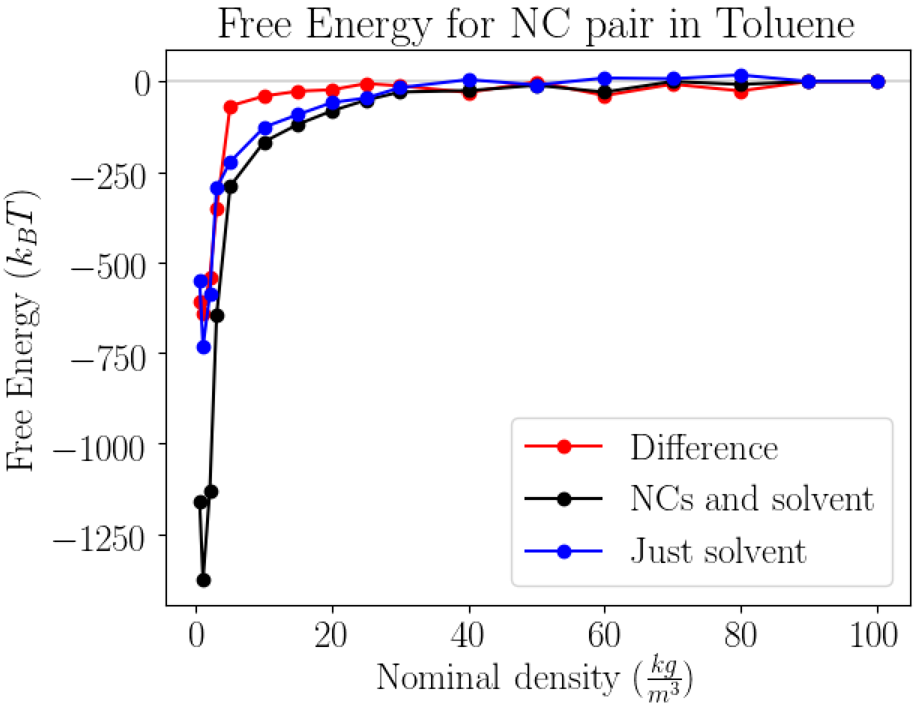


Figure S12: The Free energy of the NC pair and solvent system (black), compared with that of a system composed of just solvent (blue), and the difference betweeen the two (red).