

Supporting information for:

Enthalpy and Entropy of Nanoparticle Association

from Temperature-dependent Cryo-TEM

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Derivation of the equilibrium distribution of linear aggregates of nanoparticles

Using the Flory-Huggins approximation, the equilibrium size distribution of linear nanoparticle assemblies is derived by statistical mechanics. Our conclusions agree with the results of Björling et al. (*J. Chem. Phys.* **1999**, *111*, 6884) for the entropy and Gibbs free energy of mixing of athermal hard spheres with large size-asymmetry.

The total free energy of a system containing nanoparticles (NPs) is given by:

$$G_{total} = \mu_{NP}N_{NP} + \mu_s N_s \quad (1)$$

Here μ is the chemical potential and N the number of nanoparticles (NP) or solvent molecules (s). For single particles, this can be rewritten as:

$$G_{total} = \mu_{NP}^0 N_{NP} + \mu_s^0 N_s + \Delta_m H - T \Delta_m S \quad (2)$$

Here μ^0 is the chemical potential of a reference system containing only single nanoparticles or solvent molecules, and the change in free energy due to the mixing of these pure systems is described by $\Delta_m H$ and $\Delta_m S$, namely, the enthalpy and entropy of mixing. Assuming that the mixing enthalpy is zero, the change in free energy purely originates from $\Delta_m S$. This assumption is reasonable because both the capping ligands at the surface of the nanoparticles and the solvent molecules have a comparable dielectric constant ($\epsilon_{Decalin} = 2.2$, $\epsilon_{OleicAcid} = 2.3$), so that the solvent-solvent, the ligand-solvent and the ligand-ligand Van der Waals interactions should all be similar to each other (per unit volume), resulting in a nanoparticle-solvent mixing enthalpy of zero. Moreover, the adsorbed ligand-solvent interactions (per unit volume) are similar for clusters and for single particles, so that the ligand-solvent interactions remain largely unchanged upon cluster formation. Therefore, the nanoparticle-solvent mixing enthalpy is not expected to appear in the final equations that describe cluster formation.

The mixing entropy is defined as the difference in the entropy before and after mixing of the 2 pure systems:

$$\Delta_m S = S_{mixed} - S_{pure} \quad (3)$$

The entropy of the pure systems is the sum of the entropy of the separate systems, S_{NP} and $S_{solvent}$. The entropy can be obtained from the number of possible indistinguishable configurations of N_{NP} single nanoparticles on a lattice, W , using Boltzmann's equation (k_B is the Boltzmann constant):

$$S = k_B \ln(W) \quad (4)$$

The number of configurations of a system is calculated based on a lattice model with N lattice sites and a lattice constant comparable to the size of a solvent molecule. A nanoparticle fills Q lattice sites.

For a system with N_s solvent molecules, the pure system is described by a lattice with $N = N_s$ lattice sites. There is but one indistinguishable configuration ($W = 1$). The entropy of the pure solvent system therefore is:

$$S_{solvent} = k_B \ln(1) = 0 \quad (5)$$

For the pure NP system, the number of configurations of N_{NP} NPs on a lattice with $N = QN_{NP}$ lattice sites is:

$$\begin{aligned} W &= (N)(N - Q)(N - 2Q) \dots (N - (N_{NP}Q + 1)) / N_{NP}! \\ &= \frac{Q^{N_{NP}} N_{NP}!}{N_{NP}!} = Q^{N_{NP}} \end{aligned} \quad (6)$$

So the entropy of the pure NP system becomes $S_{NP} = N_{NP} k_B \ln(Q)$. The total entropy of the pure phases thus is:

$$S_{pure} = S_{solvent} + S_{NP} = 0 + N_{NP} k_B \ln(Q) = N_{NP} k_B \ln(Q) \quad (7)$$

The entropy of the mixed system is calculated in a similar way as for the pure systems. For

a system containing N_{NP} nanoparticles and N_s solvent molecules, the total lattice size is $N = QN_{NP} + N_s$. The number of configurations in this system is calculated by evaluating the number of indistinguishable ways to place first the NPs and to fill the remaining lattices sites with the solvent molecules:

$$\begin{aligned}
 W &= (N)(N - Q)(N - 2Q)\dots(N - (N_{NP} - 1)Q)(N - N_{NP}Q) \times \\
 &\quad (N - N_{NP}Q - 1)\dots(1)/(N_{NP}!N_s!) \\
 &= \left[\prod_{n=1}^{N_{NP}} N_s + Qn \right] N_s!/(N_{NP}!N_s!) \\
 &= \frac{Q^{N_{NP}} \left(\frac{N}{Q}\right)!}{\left(\frac{N}{Q} - N_{NP}\right)!N_{NP}!}
 \end{aligned} \tag{8}$$

The entropy of the mixed phase thus becomes:

$$S_{mixed} = k_B \ln \frac{Q^{N_{NP}} \left(\frac{N}{Q}\right)!}{\left(\frac{N}{Q} - N_{NP}\right)!N_{NP}!} \tag{9}$$

Combining this with Eqs. (2), (3) and (7) and using the Stirling approximation ($\ln(N!) = N \ln(N) - N$) results in:

$$G_{total} = \mu_{NP}^0 N_{NP} + \mu_s^0 N_s + k_B T \left[\frac{N_s}{Q} \ln \left(\frac{N_s}{N_s + QN_{NP}} \right) + N_{NP} \ln \left(\frac{QN_{NP}}{N_s + QN_{NP}} \right) \right] \tag{10}$$

The chemical potential of the NPs is defined as:

$$\mu_{NP} = \left(\frac{\partial G_{total}}{\partial N_{NP}} \right)_{N_s} \tag{11}$$

Using Eqs. (10) and (11) the chemical potential of the nanoparticles becomes:

$$\mu_{NP} = \mu_{NP}^0 + k_B T \ln(\phi_{NP}) \tag{12}$$

Here the surface fraction ϕ_{NP} is defined as QN_{NP}/N . This chemical potential is for single particles in a solvent. The chemical potential of dimers can be estimated as being particles with an area of twice the area of a single particle. The rotational entropy is not taken into account explicitly, but is considered part of μ^0 . By following the procedure described above, the chemical potential of a dimer becomes:

$$\mu_D = \mu_D^0 + k_B T \ln(\phi_D) \quad (13)$$

This can be extended to chains containing n nanoparticles:

$$\mu_n = \mu_n^0 + k_B T \ln(\phi_n) \quad (14)$$

In chemical equilibria, the chemical potentials of the products balance those of the reactants according to the reaction stoichiometry, which holds also for nanoparticle self-assembly ($\mu_n = n\mu_1$). Combining this with Eq. (14) we can write for the equilibrium constant K :

$$K = \frac{\phi_n}{\phi_1^n} = \exp\left(\frac{n\mu_1^0 - \mu_n^0}{k_B T}\right) = \exp\left(\frac{-\Delta G^0}{k_B T}\right) \quad (15)$$

Assuming a similar free energy change for attaching a particle to a chain as for two particles forming a dimer, $\Delta G^0 = (n-1)\Delta G_2^0$, where ΔG_2^0 is the pair free energy, Eq. (15) can be rewritten as follows:

$$\ln(\phi_n) = n \left(\ln(\phi_1) - \frac{\Delta G_2^0}{k_B T} \right) + \frac{\Delta G_2^0}{k_B T} \quad (16)$$

Alternative CLD representation

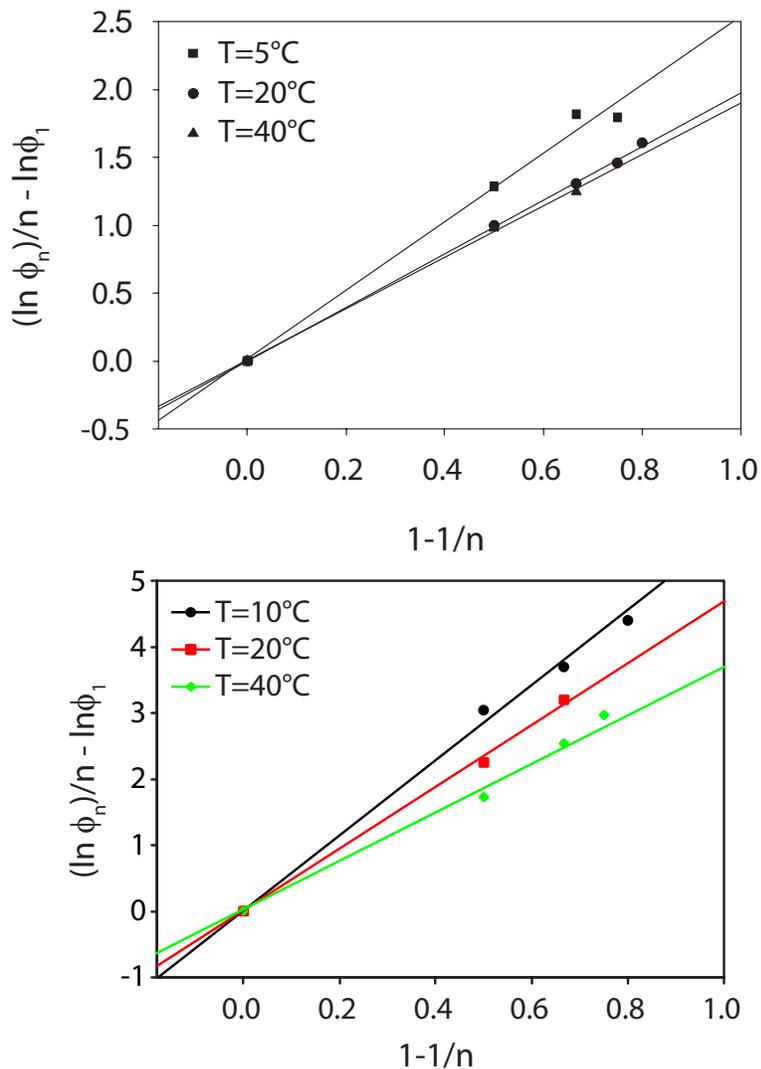


Figure S1: An alternative way to plot the CLD. In this plot the interaction free energy follows from the slope, according to the equation below. Within error, the values agree with analysis on the basis of equation 16. The first plot shows the data of the 6 nm particles and the second plot the data of the 11 nm particles.

$$\frac{\ln(\phi_n)}{n} - \ln(\phi_1) = - \left(1 - \frac{1}{n}\right) \frac{\Delta G_2^0}{k_B T} \quad (17)$$

Additional experimental data

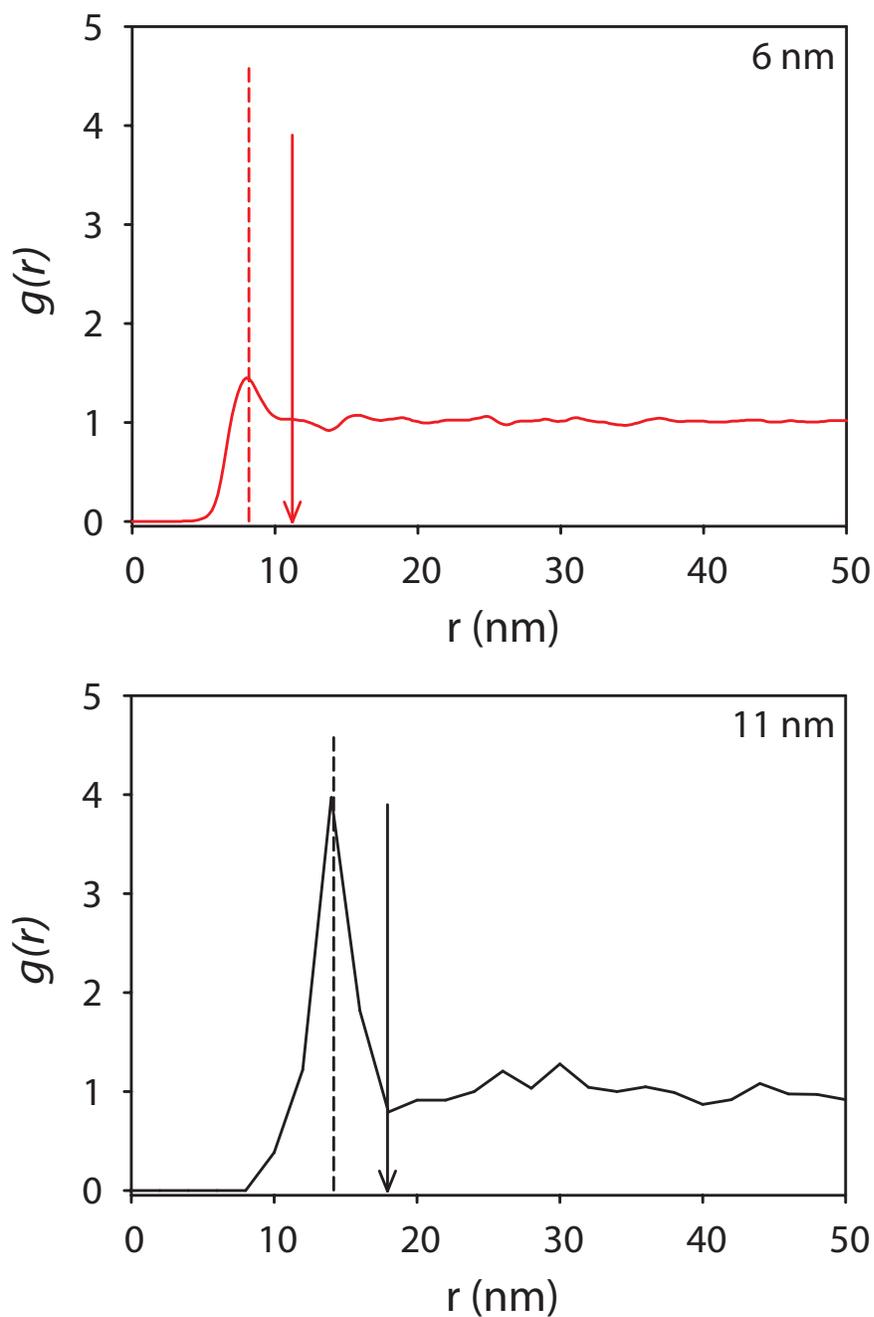


Figure S2: Radial distribution functions of PbSe nanocrystals with a diameter of 6 nm (top) and 11 nm (bottom). The dashed lines represent the effective particle diameter ($2r_{QD}$) and the arrows represent the cutoff distance (R_{co}). For the 6 nm NPs, $2r_{QD} = 9$ nm and $R_{co} = 11$ nm, and for the 11 nm NPs, $2r_{QD} = 14$ nm and $R_{co} = 18$ nm.

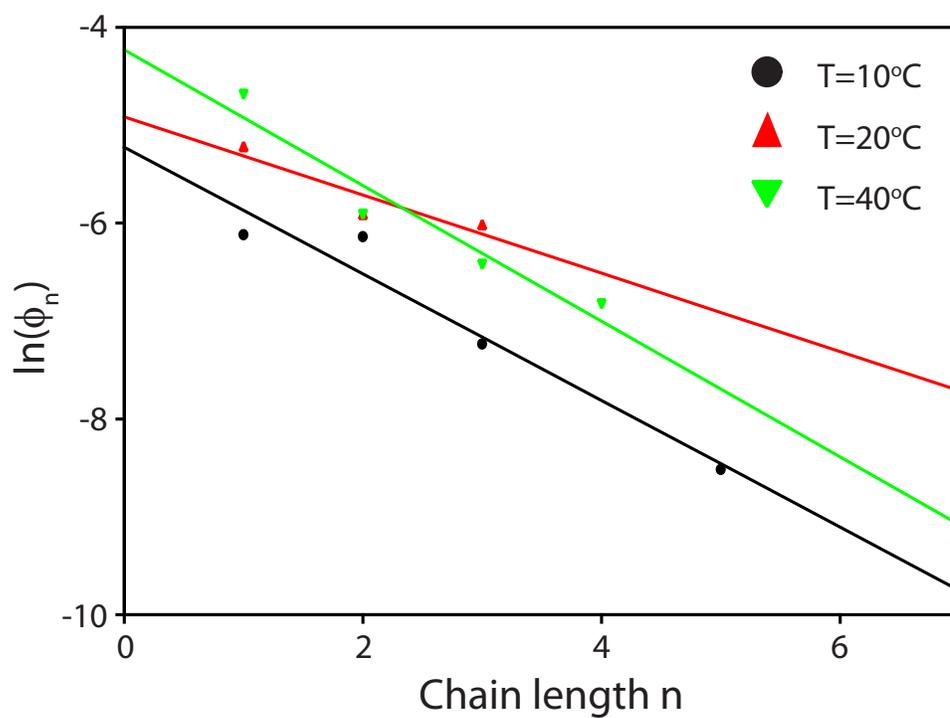


Figure S3: Chain length distribution curves for 11 nm PbSe NPs at different temperatures. Each curve is measured from a single image.

Cryo-TEM images

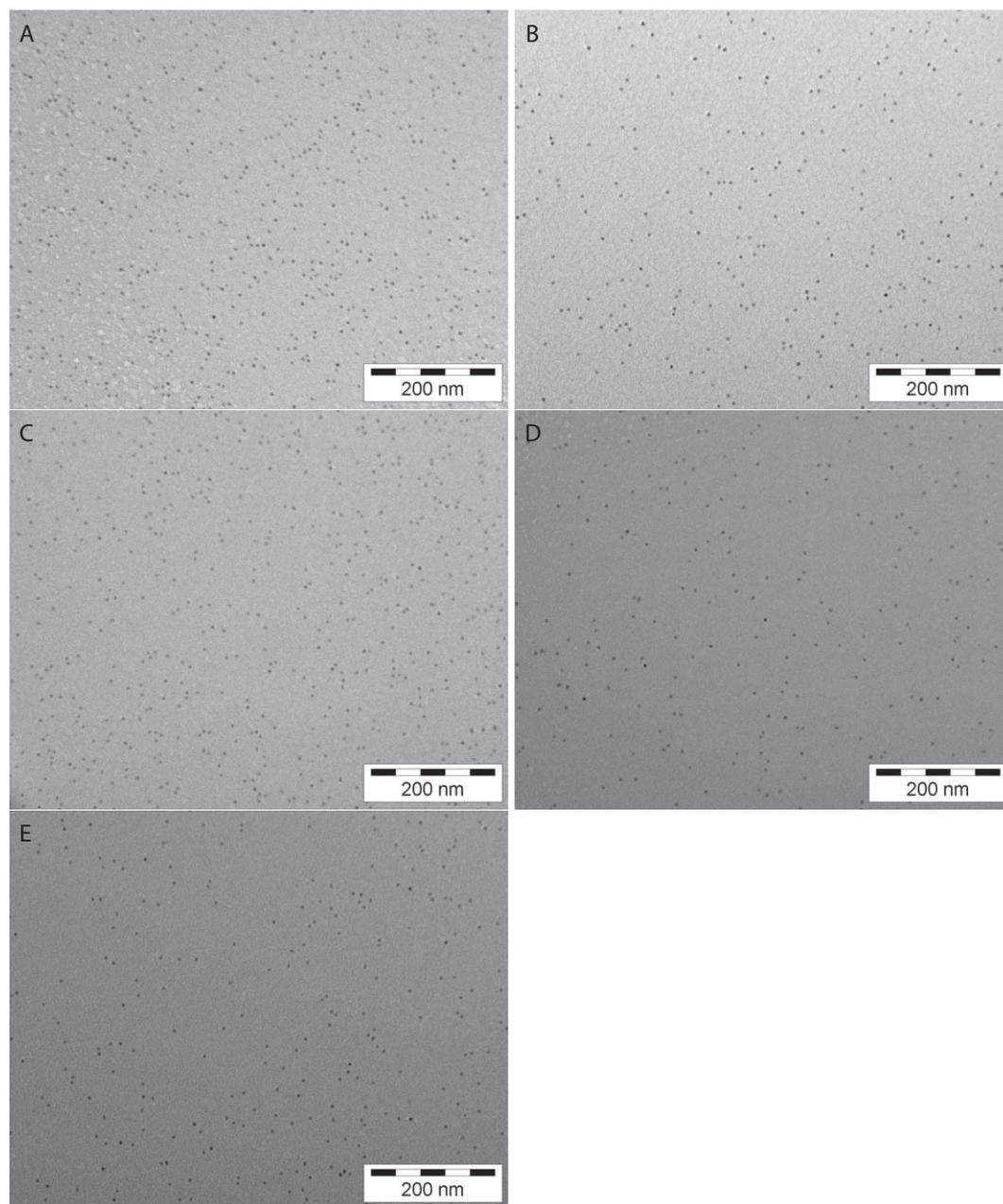


Figure S4: Selected cryo-TEM images of 6 nm PbSe NPs in decalin taken at (a) 5 °C, (b) 10 °C, (c) 20 °C, (d) 30 °C, and (e) 40 °C.

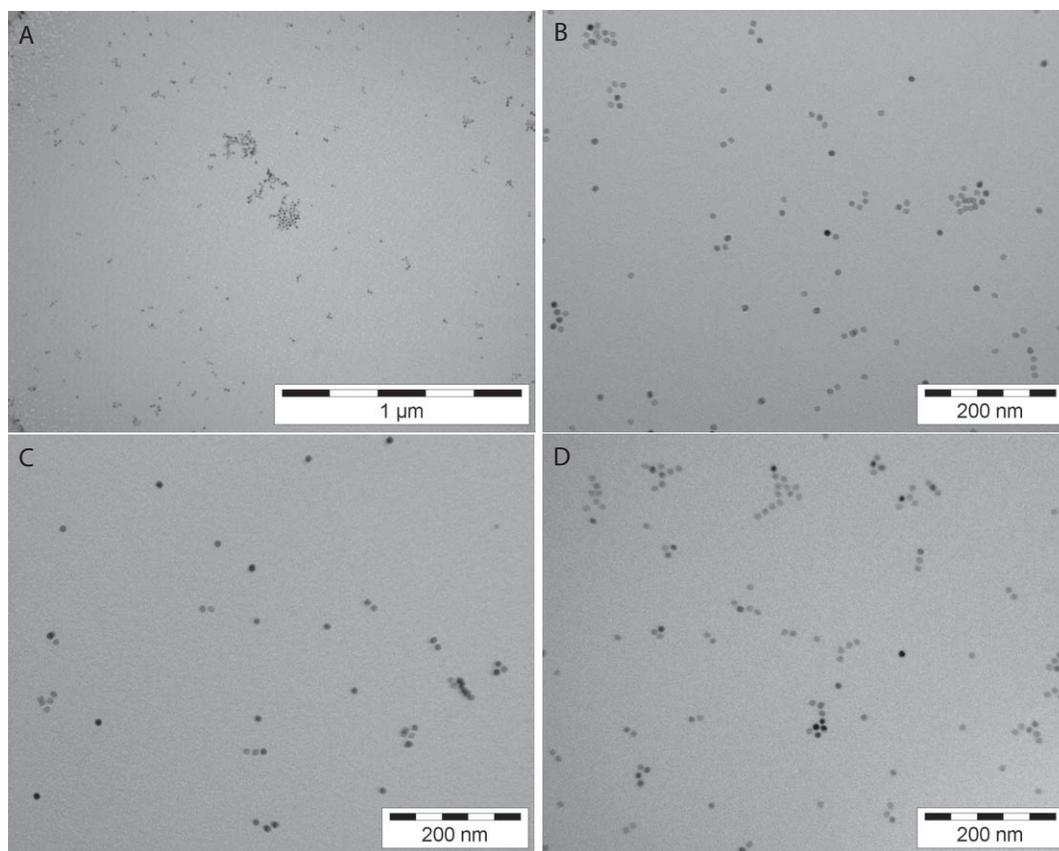


Figure S5: Selected Cryo-TEM images of 11 nm PbSe NPs in decalin taken at (a) 5 °C, (b) 10 °C, (c) 20 °C, and (d) 40 °C. Aggregates as shown in (a) do not influence the calculation of the pair free energy.