Supporting Information

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CONFINED PHASE SEPARATION OF AQUEOUS-ORGANIC NANODROPLETS

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In this DFT theory, the Helmholtz free energy contains contributions from a hard sphere reference fluid and from the attractive potential ϕ_{ij} between molecules of species i and species j.[1–3] Following Sullivan[1] and then Li and Wilemski[4], we use the Yukawa attractive pair potential,

$$\phi_{ij}(r) = -\alpha_{ij}\lambda^2 \exp(-\lambda r)/(4\pi r), \tag{1}$$

where α_{ij} is the strength parameter for the interaction between species i and j, and λ is an inverse range parameter that is assumed to be the same for all pair interactions in our model. The equilibrium density profiles are found by solving iteratively two coupled differential Euler-Lagrange equations[4],

$$\nabla^2 \mu_{hi} = \lambda^2(\mu_{hi} - \mu_i - \sum_{i,j} \alpha_{ij}\rho_j), \tag{2}$$

where μ_{hi} is the local chemical potential of species i for the hard sphere fluid , μ_i is the constant chemical potential of species i in the system. The interaction strength parameter $\alpha_{ij} = \sqrt{\alpha_{ii}\alpha jj}$ where $\alpha_{ii} = 11.102kT_{ci}\sigma_i$. The values for the Yukawa potential parameters are σ_w=0.3 nm, σ_p=0.4595 nm, T_{cw}=720 K, T_{cp}=814 K, and λ=9.889 nm^{-1}. To investigate non-spherical structures of nanodroplets, we computationally and iteratively solve Eqn.2 using finite-difference method with cylindrical coordinates.

For binary systems Eqn.2 can be rewritten as following:

$$\nabla^2 \mu_{h1}(r,z) = \lambda^2[\mu_{h1}(r,z) - \mu_1 - \alpha_{11}\rho_1(r,z) - \alpha_{12}\rho_2(r,z)] \tag{3}$$

$$\nabla^2 \mu_{h2}(r,z) = \lambda^2[\mu_{h2}(r,z) - \mu_2 - \alpha_{21}\rho_1(r,z) - \alpha_{22}\rho_2(r,z)] \tag{4}$$

where $\alpha_{12} = \alpha_{21}$, and $\rho_1(r,z)$ and $\rho_2(r,z)$ are the density profiles of species 1 and species 2, respectively.

Assuming azimuthal symmetry, Eqns. 3 and 4 can be rewritten, for binary systems, using finite-difference method over a domain of $(N+1, 2N+1)$ equally spaced mesh points so that $r = nh$ and $z = kh$ where $n = 0,1,2,....,N+1$ and $k = -N/2,....,N/2$. Thus, the Euler-Lagrange differential equations (Eqns.3, 4) become:

$$\left(\frac{1}{2nh^2} + \frac{1}{h^2}\right) g^{t+1}_{n+1,k} - \left(\frac{4}{h^2} + \lambda^2\right) g^{t+1}_{n,k} - \left(\frac{1}{2nh^2} - \frac{1}{h^2}\right) g^{t+1}_{n-1,k} = -\frac{g^t_{n,k+1} + g^t_{n,k-1}}{h^2} - \lambda^2[\mu_1 - \alpha_{11}\rho^t_1(n,k) + \alpha_{12}\rho^t_2(n,k)] \tag{5}$$

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$$\left(\frac{1}{2nh^2}+\frac{1}{h^2}\right)q^{t+1}_{n+1,k}-\left(\frac{4}{h^2}+\lambda^2\right)q^{t+1}_{n,k}-\left(\frac{1}{2nh^2}-\frac{1}{h^2}\right)q^{t+1}_{n-1,k} \quad =$$

$$-\frac{q^{t}_{n,k+1}+q^{t}_{n,k-1}}{h^2} \quad - \quad \lambda^2[\mu_2-\alpha_{21}\rho^t_1(n,k)+\alpha_{22}\rho^t_2(n,k)] \tag{6}$$

where g and q are μ_{h1} and μ_{h2}, respectively. The superscript t denotes the iteration number. Note that when $r=0$, $\mu_{hi}(n-1,k)=\mu_{hi}(n+1,k)$ by symmetry. On another hand, $\mu_{hi}(n+1,k)=\mu_{hi}(\rho_B)$ at $r=Nh$ where ρ_B represents the densities of the bulk vapor phase. Similarly, $\mu_{hi}(n,k-1)=\mu_{hi}(\rho_B)$ and $\mu_{hi}(n,k+1)=\mu_{hi}(\rho_B)$ at $z=-Nh/2$ and $z=Nh/2$, respectively.

The iterative solution process begins by using the initial trial profile for all ρ_i and ρ_j values in Eqns.(5) and (6). The equations are solved using a standard tridiagonal matrix routine where this solution then serves as the next trial profile. The initial density profiles are based on CS or WM structures that are somewhat larger than the final RDS structure. These profiles quickly creep to those of the RDS structure during the iterations and then remain stationary. If the initial structures are too small, no stationary solution is found. The initial density profiles shrink away completely. The iteration procedure is terminated when the difference between successive iterates becomes less than a prescribed limit Δ. For our DFT calculations, typical parameter values are $N=4001$, $r=7.5$ nm, $z=15$ nm.

References

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