Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electron transfer in nonpolar media: Electronic supplementary information (ESI)

Dmitry V. Matyushov[1]
Department of Physics and School of Molecular Sciences, Arizona State University, PO Box 871504, Tempe, AZ 85287-1504 [a]

I. SIMULATION PROTOCOL

Monte Carlo (MC) simulations of solvation applied the standard Metropolis sampling[1] as implemented in our previous studies.[2] The solvent-solvent interactions were taken in the Lennard-Jones (LJ) form

$$U_{ss}(r) = 4\epsilon_{\mathrm{lJ}}\left[(\sigma_{\mathrm{LJ}}/r)^{12} - (\sigma_{\mathrm{LJ}}/r)^{6}\right] \tag{S1}$$

The solute was viewed as a hard-sphere core with the radius $a = R + \sigma_{\mathrm{LJ}}/2$, where the solvent diameter was identified with its LJ diameter $\sigma_s = \sigma_{\mathrm{LJ}}$. The attractive solute-solvent interaction was taken in the form of the induction free energy

$$\beta F_{ei} = -\tfrac{1}{2}(z^*)^2\alpha^* \sum_j (\sigma_s/r_j)^4, \tag{S2}$$

where r_j is the distance between the solute fixed at the center of the simulation box and the solvent molecule. Further, the sum runs over the N molecules of the solvent, $\alpha^* = \alpha/\sigma_s^3$, and $(z^*)^2 = \beta(ze)^2/\sigma_s$.

The MC simulations were performed for a cubic simulation box with $N = 500$ molecules and the reduced density $\rho^* = \rho\sigma_s^3 = 0.8$. Three values of the temperature-scaled LJ energy $\beta\epsilon_{\mathrm{LJ}}$ were adopted in simulations including the solute in the simulation box: 0.125, 0.5, and 1.0; 6 values of $\beta\epsilon_{\mathrm{LJ}}$ were used in the simulations of the pure LJ liquid. The reduced polarizability α^* was altered in the simulations in the range between 0.02 and 0.1. The typical length of simulations was $\sim 10^6$ configurations of the entire simulation box. Test runs with $N = 862$ solvent particles in the simulation box were carried out. They produced the results virtually indistinguishable from those with $N = 500$ solvent particles.

II. STRUCTURE FACTORS

The derivations presented in the main text are based on approximating the density-density structure factor of a liquid with the corresponding structure factor of a Percus-Yevick (PY) hard-sphere (HS) fluid.[3] The $k = 0$ value of the HS structure factor $S(k)$ is fixed by the isothermal compressibility β_T of the liquid through $S(0) = k_{\mathrm{B}}T\rho\beta_T$. The structure factors of fluids with more complex interaction potentials will deviate from the structure factors of the HS fluid and here we test this approximation by using the structure factors for a number of LJ liquids simulated with the MC protocol.

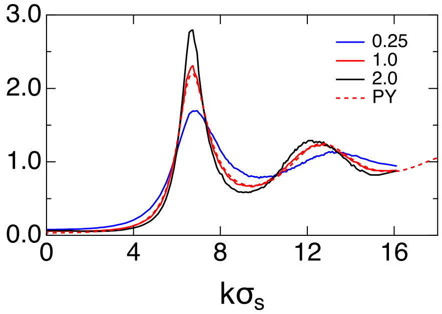

Figure S1. $S(k)$ for LJ liquids at $\beta\epsilon_{\mathrm{LJ}}$ values indicated in the plot and PY HS structure factor at $\rho^* = 0.8$ corresponding to the simulation conditions (red dashed line).

The structure factors[3,4]

$$S(k) = N^{-1}\langle \rho_{\mathbf{k}}\rho_{-\mathbf{k}}\rangle \tag{S3}$$

were calculated from the reciprocal-space density $\rho_{\mathbf{k}}$ on the lattice vectors of the simulation box[5] $\mathbf{k} = (2\pi/L)\mathbf{n}$ for a cubic simulation box with the side length L; $\mathbf{n} = \{n_x, n_y, n_z\}$ are non-negative integers excluding the point $k = 0$. The range of k-values is limited by the lowest $k_{\mathrm{min}} = 2\pi/L$ available for a finite-size simulation box. The $k = 0$ value, as well as $S(k)$ at $k < k_{\mathrm{min}}$, were obtained by linear fitting of $S(k)^{-1}$ to k^2 at a number of lowest values of k provided by the lattice vectors. The results for a number of scaled LJ energies $\beta\epsilon_{\mathrm{LJ}}$ is shown in Fig. S1. Simulation trajectories with the values $\beta\epsilon_{\mathrm{LJ}}$ equal to 0.125, 0.25, 0.5, 1.0, 1.5, 2.0 were produced for this calculation.

Figure S1 shows $S(k)$ produced by simulations in comparison to the PY HS structure factor at ρ^* used in simulations. It is clear that low-k behavior of LJ $S(k)$ deviates from the HS result. Therefore, the packing density in the HS structure factor was adjusted to fit $S(0)$ for LJ liquids according to the equation

$$S(0) = S_{\mathrm{PY}}(0) = (1-\eta)^4/(1+2\eta)^2. \tag{S4}$$

The adjusted PY structure factors were used in the k-integration as described in the main text. Briefly, we assume that $g_{0s} = \theta(r-a)$, which produces the function

$$f_3(k\sigma_s, a/\sigma_s) = \frac{1}{\sigma_s^2}\int_{a/\sigma_s}^{\infty} \frac{dx}{x^3}\sin(k\sigma_s x). \tag{S5}$$

Further, one obtains for $F(k\sigma_s)$ in eqn (35) in the main text $(z = 1)$

$$F(k\sigma_s) = \frac{\sigma_s^5}{(4\pi)^2} f_3^2(k\sigma_s, a/\sigma_s). \tag{S6}$$

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[a] Electronic mail: dmitrym@asu.edu

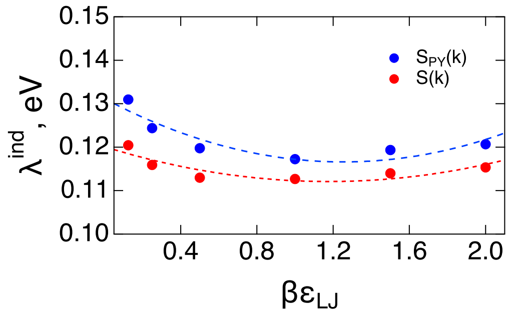

Figure S2. $\lambda^{\rm ind}$ for LJ liquids vs $\beta\epsilon_{\rm LJ}$ calculated from eqn (S7) with $S(k)$ from MC simulations and from PY HS structure factor with the packing fraction adjusted to match $S(0)$ from simulations (eqn (S4)).

Finally, one obtains for the reorganization energy

$$\lambda^{\rm ind} = \frac{9\beta e^4}{\rho^* \sigma_s^2}\left(\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\right)^2 \int_0^\infty F(x)S(x)dx, \tag{S7}$$

where the integration variable is $x = k\sigma_s$. The results of this integration are shown in Fig. S2 for $\sigma_s = 5.4$ Å and $\epsilon_\infty = 2.12$ (parameters for $\mathrm{CCl_4}$).

Figure S2 shows the results of integration in eqn (S7) with $S(k)$ from MC simulations and by using the density-adjusted PY HS structure factors. The deviation between two sets of results ranges from 8% at a somewhat unrealistic $\beta\epsilon_{\rm LJ} = 0.125$ to 3% at the more realistic $\beta\epsilon_{\rm LJ} \simeq 1 - 2$.

Equation (S7) can be compared to eqn (45) in the main text introducing the empirical parameter κ

$$\lambda^{\rm ind} = \frac{3\beta e^4 (2z-1)^2}{320\eta}\kappa\left(\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\right)^2 \frac{\sigma_s^3}{a^5}. \tag{S8}$$

Comparing eqn (S7) to eqn (S8) leads to κ ranging from 0.3 to 0.27 in the entire range of LJ energies simulated here.

III. RESULTS

In terms of the reduced parameters used in the simulation protocol, the average induction interaction is given as

$$\beta\langle V\rangle = 2\pi\rho^*\alpha^*(z^*)^2(\sigma_s/a), \tag{S9}$$

where $V = \sum_j \alpha e^2/(2r_j^4)$. As is discussed in the main text, $\langle\Delta F_e\rangle_1 = \langle V\rangle + 2\lambda^{\rm ind}$ at $z = 1$. The induction reorganization energy is given by the following relation

$$\beta\lambda^{\rm ind} = (\pi/10)\kappa(z^*)^4(\alpha^*)^2\rho^*(\sigma_s/a)^5, \tag{S10}$$

where the empirical parameter κ describes the reduction from the full k-integration with the density structure factor $S(k)$ to the approximation $S(k) = \kappa$. This approximation puts $S(k)$ between its limits $S(0) \ll \kappa$ and $S(\infty) = 1$.

The reduced form for the structure factor leading to eqn (S10) does not affect its dependence on temperature, which follows the inverse temperature scaling $\lambda^{\rm ind} \propto T^{-1}$ at $a \simeq \sigma_s$. This is illustrated in Fig. S3 where the direct numerical integration of the PY structure factor is compared with eqn (S10) at the fixed value of $\kappa = 0.31$.

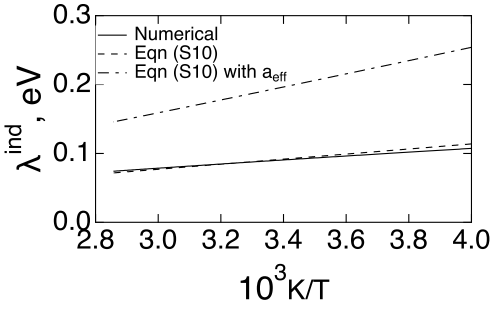

Figure S3. $\lambda^{\rm ind}$ vs $1/T$. Solid line shows the numerical integration using the PY structure factor in eqn (28) in the main text with the step-function solute-solvent pair distribution function. This calculation is compared to eqn (S10) with $\kappa = 0.31$ and $a_{\rm eff} = a$ (dashed line). The dash-dotted line shows the same result with $a_{\rm eff}$ calculated from eqn (S12).

IV. EFFECTIVE SOLUTE RADIUS

The effective radius of the solute can be expressed as the integral with the solute-solvent pair distribution function $g_{0s}(r)$

$$a_{\rm eff}^{-5} = 5\int_0^\infty (dr/r^6) g_{0s}(r). \tag{S11}$$

It transforms to the perturbation integral expressed in terms of the dimensionless distance variable $x = r/\sigma_s$ and the reduced density ρ^* when the hard-sphere function is used for $g_{0s}(r)$

$$a_{\rm eff}^{-5} = \sigma_s^{-5} I_6^{(2)}(\rho^*, r_{0s}), \quad I_6^{(2)}(\rho^*, r_{0s}) = 5\int_0^\infty \frac{dx}{x^6} g_{0s}(x). \tag{S12}$$

The perturbation integral $I_6^{(2)}(\rho^*, r_{0s})$ is a function of two parameters only: the reduced density $\rho^* = \rho\sigma_s^3$ and $r_{0s} = R/\sigma_s + 1/2$. This function was tabulated in Ref. 6 in the form

$$I_6^{(2)}(\rho^*, r_{0s}) = \frac{a(\rho^*)}{r_{0s}^5} + \frac{b(\rho^*)}{r_{0s}^6} + \frac{c(\rho^*)}{r_{0s}^7} + \frac{d(\rho^*)}{r_{0s}^8}. \tag{S13}$$

The nominators in this expansion are polynomials of the reduced density given by the following equations

$$\begin{aligned} a(\rho^*) &= 1 + 0.586\rho^* - 1.390(\rho^*)^2 + 0.776(\rho^*)^3 \\ b(\rho^*) &= 1.062\rho^* + 4.608(\rho^*)^2 - 2.964(\rho^*)^3 \\ c(\rho^*) &= -0.970\rho^* - 4.134(\rho^*)^2 + 3.798(\rho^*)^3 \\ d(\rho^*) &= 0.241\rho^* + 1.194(\rho^*)^2 - 1.393(\rho^*)^3 \end{aligned} \tag{S14}$$

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