Universal iso-density polarizable continuum model for molecular solvents

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Implicit electron-density solvation models based on joint density-functional theory offer a computationally efficient solution to the problem of calculating thermodynamic quantities of solvated systems from first-principles quantum mechanics. However, despite much recent interest in such models, to date the applicability of such models to non-aqueous solvents has been limited because the determination of the model parameters requires fitting to a large database of experimental solvation energies for each new solvent considered. This work presents an alternate approach which allows development of new solvation models for a large class of protic and aprotic solvents from only simple, single-molecule \textit{ab initio} calculations and readily available bulk thermodynamic data. We find that this model is accurate to nearly 1.7 kcal/mol even for solvents outside our development set.

Keywords: Density Functional Theory, Quantum Chemistry, Polarizable Continuum Model
I. INTRODUCTION

*Ab initio* methods, in particular density-functional theory, have a well established record of significant impact in chemistry, physics and materials science. However, despite the fact that many chemical reactions occur in a liquid environment where the solvent (or electrolyte) plays an important role in the chemistry, applications of density-functional methods to liquid and solvation chemistry has lagged behind applications to solids, gas-phase molecules, or surfaces in vacuum. This is because a single configuration of liquid molecules is often not representative of the thermal average, and thermodynamic sampling, done for instance with *ab initio* molecular-dynamics or QM/MM, is needed to carry out realistic calculations.

Joint density-functional theory (JDFT) takes equilibrium properties of the liquid environment (such as mean molecular density) and solute (mean electron density) as the independent variables and gives direct access to free-energies, thus removing the need for thermodynamic sampling and integration and providing an economic alternative to molecular dynamics. Polarizable continuum models (PCMs) are one class of approximation where the solvent effect is reproduced with an effective dielectric description of the liquid environment. Among these models, isodensity PCMs, which are based on the solute electron density and thus represent a particular class of approximate joint functionals within the JDFT framework, have achieved significant success in describing processes in aqueous environments, including predicting, among other things, solvation energies for molecules and ions as well as interfacial capacitances and potentials of zero charge for crystalline metals. Successful application of *ab initio* methods coupled to such continuum descriptions of the solvent has great potential for new discoveries in many areas of research, including biochemistry and energy-material related technologies.

Despite much recent interest, one important obstacle is that most isodensity PCMs are parametrized for aqueous solutions, but not for many other solvents commonly encountered in organic chemistry and electrochemistry. There has been much progress in reducing empiricism and increasing the generality of such models, but such approaches continue to require that multiple solvent-dependent parameters be fit to experimental data sets, typically to solvation free-energies of molecules.

While a great deal of solvation data is available for common solvents such as water, chloroform and carbon tetrachloride, many solvents of technological relevance do not have...
sufficient published data from which to construct continuum models. To aid exploration of microscopic physical processes in general solvent environments and particularly studies to identify to best solvent for a given application, this work provides a general framework for constructing accurate models for a large class of solvents using a limited number of coefficients, all of which can be obtained directly either from bulk thermodynamic data that is generally easy to obtain or from relatively simple single-molecule ab initio calculations.

II. UNIVERSAL SOLVATION MODEL

Polarizable continuum models represent a class of approximate joint density-functional theories which treat the interaction with the fluid environment as the dielectric response of a continuum medium filling the space not occupied by the molecule or surface of interest, to which we refer hereafter generically as the “solute”. For most solvents, the dielectric response of the fluid is the largest, but not the entire, contribution to the free energy of solvation. This response is generally approximated by the electrostatic interaction of the total (ionic and electronic) solute charge distribution with the surrounding medium, whose response is taken to be that of a continuum dielectric. Most such models assume that the dielectric response of the fluid is linear; but this need not be so. Indeed, in this work, we use the nonlinear dielectric response function of Gunceler et. al., which includes the rotational dielectric saturation of polar solvents. The advantage of using a nonlinear response description is that, compared to a linear model, the nonlinear response is able to include more physics into the solvation model without introducing additional fit parameters. Continuum solvation models generally treat the remaining, non-electrostatic contributions to the free energy as related to the total area of the solute-solvent interface, whose form is independent of the underlying dielectric response model. The central ideas in this paper thus apply equally well to linear response models, should one desire to work with those instead.

The first key issue in development of a PCM approximation to a full, joint density-functional theory is determination of the dielectric region. Traditionally, continuum models filled space with the dielectric medium except for spherical cavities centered on each atom of the solute, each with a species-dependent atomic radius ultimately fit to a database of solvation energies. Several groups, instead, independently developed the isodensity approach for cavity determination, where the dielectric function changes from 1 in the
interior of the solute region to the bulk value ($\varepsilon_{\text{bulk}}$) of the solvent dielectric constant, with the transition occurring on the surface of a critical cutoff $n_c$ of the solute electron density. As noted by Petrosyan et al., this has the advantage of placing such models in the class of approximate joint density-functionals.

For the functional form of the above transition in the dielectric response, we here use the functional form of Petrosyan et al.,

$$\varepsilon(\vec{r}) = 1 + (\varepsilon_{\text{bulk}} - 1) s(n(\vec{r})), \quad (1)$$

where $s(n(\vec{r}))$ is the cavity-shape function,

$$s(n(\vec{r})) = \frac{1}{2} \text{erfc} \left( \frac{\log(n(\vec{r})/n_c)}{\sigma \sqrt{2}} \right). \quad (2)$$

The parameter $\sigma$, controlling the width of the transition, is chosen to be large enough to resolve the transition on typical real-space grids employed in density-functional calculations yet small enough that the results are insensitive to the specific value employed. (Here, we employ $\sigma = 0.6$ as chosen by Petrosyan and coworkers.) By replacing atom-dependent fit parameters with a single critical electron density $n_c$, which can then be fit to a database of solvation energies for each solvent considered, such iso-density approaches thereby eliminate many fit parameters in favor of a single parameter. However, the remaining cutoff parameter $n_c$ is clearly highly solvent dependent, varying over several orders of magnitude (see Table I in main text and the supplementary information), and still requires access to a database of solvation energies to find the best fit for each new solvent considered.

Even beyond the fitting needed to determine $n_c$, additional key parameters must be determined to yield accurate solvation energies. This is because significant non-electrostatic processes contribute to solvation, such as the dispersion interaction between the solute and solvent, as well as the free-energy associated with forming the cavity in the solvent. This is particularly true for non-aqueous solvents like chloroform and carbon tetrachloride, where solvation energies are not dominated by electrostatic interactions. To capture these effects, the effective surface-tension approximation, first developed by Andreussi et al. and later modified by Gunceler et al., approximates the non-electrostatic contributions to the solvation energy ($E_{ne}$) as the effective surface area of the solute molecule ($A$) multiplied by an effective surface tension ($\tau_{\text{eff}}$),

$$E_{ne} = \tau_{\text{eff}} A,$$
where the effective surface area is calculated from the cavity shape function \(s(n(\vec{r}))\) as
\[
A = \int d^3\vec{r} |\nabla s|,
\]
and the effective surface tension \(\tau_{\text{eff}}\) is a second parameter to be fit to the solvation-energy database.

Table I gives typical values for the iso-density \(n_c\) and effective surface tension \(\tau_{\text{eff}}\) parameters, which we determined for six solvents from fits to solvation energy data. The table indicates a clear trend in the effective surface tensions. For solvents with high bulk surface tension (such as water), the effective surface tension generally is positive, whereas, for a large number of non-polar and weakly polar solvents with weak bulk surface tensions and strong (attractive) dispersion interactions, these effective surface tensions can become negative.

Motivated by the observation of a consistent trend of the effective surface tension with the strength of dispersion interactions, we now consider whether there exists a simple, approximate universal correlation between these two quantities. To begin, we separate out the bulk surface tension, as suggested independently by Dupont and coworkers\(^8\), and write \(\tau_{\text{eff}} = \tau_{\text{bulk}} + \tau'\), where \(\tau_{\text{bulk}}\) is the (generally available) bulk surface tension of the solvent and \(\tau'\) is the correction term for microscopic size effects, which we will now attempt to correlate with dispersion interactions. Next, to quantify the strength of the dispersion interactions, we make use of a very simple model where the van der Waals \(r^{-6}\) potential has been integrated in a region outside twice the van der Waals radius of the solvent, resulting in a dispersion energy per unit area \(E_{\text{vdw}}/A \equiv \tau_{\text{vdw}}\) of
\[
\tau_{\text{vdw}} = \frac{s_6}{A} \int_{2R_{\text{vdw}}}^{\infty} 4\pi r^2 dr \frac{N_{\text{bulk}} \sqrt{C_6 C_6}}{r^6} \\
= \gamma_1 \left[ \frac{N_{\text{bulk}} C_6}{R_{\text{vdw}}^5} \right],
\]
where we employ the pair-potential model of dispersion corrections introduced by Grimme\(^{21}\). Here, \(C_6\) is the effective dispersion coefficient described by Grimme, \(N_{\text{bulk}}\) is the bulk density of the solvent, \(R_{\text{vdw}}\) is a measure for the size of the solvent molecule and \(s_6\) is a dimensionless scale factor accounting for renormalization of the fluctuating dipole interaction by multiple-atom interactions. Finally, in the second line of equation \(3\), we absorb \(s_6\) and all other dimensionless constants into \(\gamma_1\). (See below for a more detailed exploration of \(s_6\).)

Figure 1 shows that there indeed is a strong correlation between the correction term \(\tau' = \tau_{\text{eff}} - \tau_{\text{bulk}}\) and our measure of dispersion strength \(N_{\text{bulk}} C_6/R_{\text{vdw}}^5\). The only apparent
FIG. 1. Surface tension correction \( \tau' = \tau_{\text{eff}} - \tau_{\text{bulk}} \) as a function of Van der Waals factor \( N_{\text{bulk}} C_6 / R_{vdw}^5 \) (scaled to that of water to provide a dimensionless quantity for display purposes): data from fits to experimental solvation energies\(^{15,18}\) (black x’s), best-fit linear correlation in the form of equation \( 3 \) (red line).

Outlier in the fit set is CS\(_2\), whose anomalous behavior we suspect is related to its being the only molecule in the set which is both highly polar and has no net dipole moment. Finally, we note that the form of the correlation is nearly perfectly linear.

Based on the above observations, we propose as an approximate universal form for the total effective cavity tension

\[
\tau_{\text{eff}} = \tau_{\text{bulk}} + \gamma_0 + \gamma_1 \left[ \frac{N_{\text{bulk}} C_6}{R_{vdw}^5} \right],
\]  

(4)

where the first term \( \tau_{\text{bulk}} \) is the bulk surface tension of the solvent and is a measure of the energy cost to form macroscopic cavities in the liquid, the second term \( \gamma_0 \) is a microscopic size correction corresponding to the vertical intercept of the linear correlation, and the final term incorporates the effects of long-range dispersion as the slope of the correlation. Table \( \text{I} \) gives our best fit values for \( \gamma_0 \) and \( \gamma_1 \) and compares the resulting linear model values for \( \tau_{\text{eff}} \).
with those which came from the original data-set fits, showing that we indeed can predict quite well appropriate values for this parameter without fitting to solvation data whatsoever.

Regarding the magnitude of our slope fit parameter $\gamma_1$, comparing equations $3$ and $4$ we are able to extract from our fit a measure of the Grimme van der Waals scale factor, $s_6 = 32 \times 3 \times \gamma_1 = 1.26$. To place this value for $s_6$ in context, we note that, in the Grimme framework $^{21}$, this parameter is generally fit to account first for the fact that some of the dispersion interaction (the short-range part) is accounted in standard approximate exchange-correlation functionals and, second, for the fact that a pair-potential model for the van der Waals interaction misses multiple molecule interactions. Ideally, the $s_6$ parameter would have a value of unity, but is known to change by as much as 45% between different electronic exchange-correlation functionals $^{21}$, placing our fit result squarely in the expected range.

In addition to the readily available bulk surface tension $\tau_{\text{bulk}}$, we require three solvent-dependent quantities to determine $\tau_{\text{eff}}$, namely the bulk number density of the solvent $N_{\text{bulk}}$ (readily available from bulk thermodynamic data), the effective Van der Waals coefficient $C_6$ (readily computed from static dipole polarizabilities of each atom and available in tabulated form $^{21}$), and the effective Van der Waals radius of the solvent $R_{\text{vdw}}$, which can be obtained for most solvents from the Van der Waals equation-of-state for the gas phase or, as the next section describes, computed readily from simple $ab$ initio calculations of a single molecule.

To complete our model, once $\tau_{\text{eff}}$ is known, the one remaining parameter $n_c$ can then be constrained by the self-solvation energy, which can be easily determined from the vapor pressure $^{22}$, another readily available bulk thermodynamic datum. The fourth column of Table I lists the $n_c$’s and $\tau_{\text{eff}}$ determined from our model for the six solvents in our original fit set. Parameters for nine additional solvents of technological importance are reported in table 3 of the supplementary information.

The above determination of the isodensity contour $n_c$ from the self-solvation energy requires computing the total solvation energy as a function of $n_c$. In addition to the non-electrostatic contributions, captured by the effective surface tension as described above, our model requires also the electrostatic contributions. For these electrostatic interactions, we employ the non-linear dielectric response model of Gunceler et al $^{23}$. This model requires solvated dipole moments, which we have determined self-consistently within our model fluids. (Results for each molecule are tabulated in the supplementary materials.) We find that,
within our fit set, there is a modest increase in the root mean-square (rms) error for solvation energies to 1.40 kcal/mol as we move away from direct fitting to solvation energies within each solvent separately and employ our universal approach which uses only our model for $\tau_{\text{eff}}$ and the self-solvation energy. (Again, CS$_2$ is the one clear outlier.)

Finally, after completing our universal model, we discovered solvation energies for four additional solvents not included in our fit set (figure 2). Employing the same value for the universal parameters $\gamma_0$ and $\gamma_1$, readily available experimental data for the density, vapor pressure, and dielectric constant, and ab initio results for the molecular polarizability and van der Waals radius, we find again a quite encouragingly small rms solvation error of 1.66 kcal/mol for the predicted solvation energies in these new solvents. These results are encouraging, given that they come from a universal model which requires no solvation data for fitting whatsoever.

### III. AB INITIO METHOD FOR VAN DER WAALS RADII

As stated earlier, the van der Waals radius of a solvent is one of the parameters which determine our universal solvation model. This parameter typically comes from the volume of exclusion in the Van der Waals equation of state. Such data is available for many gasses and

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**TABLE I.** PCM parameters for the solvents used in the determination of the values for $\gamma_0$ and $\gamma_1$ (Figure 1).

| Solvents          | $n_c$ | $\tau_{\text{eff}}$ | Error | $\gamma_0$ | $\gamma_1$ | Mean error: |
|-------------------|-------|----------------------|-------|-------------|-------------|-------------|
|                   | (a$_0^{-3}$) | (E$_H$/a$_0^{-2}$) | (kcal/mol) | (a$_0^{-2}$) | (E$_H$/a$_0^{-2}$) | (kcal/mol) |
| Water             | 1.0 x 10$^{-3}$ | 9.50 x 10$^{-6}$ | 0.95 | 9.0 x 10$^{-4}$ | 1.02 x 10$^{-5}$ | 1.38 |
| Chloroform        | 2.4 x 10$^{-5}$ | -9.23 x 10$^{-6}$ | 0.82 | 5.6 x 10$^{-4}$ | -1.11 x 10$^{-5}$ | 1.30 |
| Carbon tetrachloride | 1.2 x 10$^{-4}$ | -8.99 x 10$^{-6}$ | 1.06 | 2.9 x 10$^{-4}$ | -8.61 x 10$^{-6}$ | 1.21 |
| Isobutanol        | 1.5 x 10$^{-3}$ | -8.96 x 10$^{-6}$ | 0.76 | 1.8 x 10$^{-3}$ | -8.28 x 10$^{-6}$ | 0.83 |
| Carbon disulfide  | 2.9 x 10$^{-5}$ | -7.96 x 10$^{-6}$ | 1.01 | 3.4 x 10$^{-4}$ | -1.32 x 10$^{-5}$ | 2.32 |
| Ethyl ether       | 2.6 x 10$^{-4}$ | -1.08 x 10$^{-5}$ | 1.13 | 5.0 x 10$^{-4}$ | -1.12 x 10$^{-5}$ | 1.35 |

$\gamma_0 = -1.927 \times 10^{-5} \ E_H/a_0^{-2}$  $\gamma_1 = -1.313 \times 10^{-2}$  Mean error: 1.40
FIG. 2. Error in solvation energies for four solvents (dichloromethane, DMSO, ethanol and THF), none of which were used in the fitting set. Root mean-square error is 1.66 kcal/mol. Parameters for each solvent can be found in the supplementary information.

vapors of common solvents, but not for all solvents of technological importance. Motivated by this, we use the shape function (eq 2), with a new critical density parameter $n_{vdW}$, to define a Van der Waals radius,

$$R_{vdw} = \sqrt{\frac{3}{4\pi} \int d^3r \ s(n(r))},$$  \tag{5}

where for $n_c$ we employ the value $n_{vdW} = 1.83 \times 10^{-4} \ a_0^{-3}$, which was obtained by fitting to published van der Waals radii available in the literature. Figure 3 compares the accepted values with our model values, showing excellent agreement with an rms error of only 0.1 Å. (Numerical values for each solvent molecule are available in the supplemental information.)

IV. CONCLUSION

In conclusion, this work presents a universal isodensity solvent model which predicts solvation energies to near chemical accuracy for a wide range of polar and nonpolar solvents.
FIG. 3. Experimental versus density-functional predicted values (eq 5) of the van der Waals radius for molecules listed in the supplemental information.

based only on readily obtainable bulk thermodynamic data and ab initio computables, without the need for a database of solvation energies to fit the model parameters for each new solvent of interest. What makes this possible is an empirically observed correlation between the microscopic corrections to the cavity surface-tension parameter and the $C_6$ van der Waals coefficient. The observed correlation allows just two parameters ($\gamma_0$ and $\gamma_1$), once fit to solvation data for a training set of six solvents, to determine the needed microscopic surface tension parameter for any new molecular solvent to be considered. Finally, we show how the one remaining parameter in our model, the isodensity contour $n_c$ that defines the solute cavity, may be obtained from vapor-pressure data, which is generally more available
than an extensive database of solvation energies.

For the six solvents of the training set, rms error in solvation energies is 1.40 kcal/mol, and, for four solvents for which we discovered data after fixing the model parameters, we find only a modest increase in the rms error to 1.66 kcal/mol. This work thus opens to \emph{ab initio} investigation a wide range of solvents previously inaccessible to such solvation studies, opening new application areas in chemistry, biology and physics to \emph{ab initio} study.

V. COMPUTATIONAL METHOD

We performed all calculations with JDFTx\textsuperscript{25}, an open-source implementation of joint density-functional theory. We employed the revTPSS meta-gga approximation\textsuperscript{26} for the electronic exchange-correlation and norm-conserving pseudopotentials obtained from the Opium pseudopotential generation package\textsuperscript{27} to represent the ionic cores. Kohn-Sham orbitals are expanded using planewaves up to a cutoff of 30 Hartrees. Finally, we obtained molecular geometries from the CCCBDB database\textsuperscript{28}, and produced ball-and-stick figures using the Avogadro package\textsuperscript{29}.

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See supplemental material at [URL will be inserted by AIP] for the tables of Van der Waals radii, effective dipole moments and parameters for additional solvents.

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