On the stability criteria of the Kirkwood–Riseman diffusion tensor

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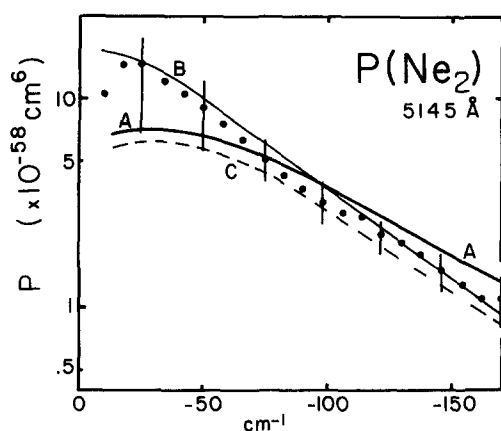
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FIG. 2. The *polarized* neon diatom Raman spectrum.

dence of the polarizability, which was not accounted for. For comparison, curve B represents an empirical fit previously obtained.[9] Curve C is based on an earlier SCF computation,[1] and curve D on the classical DID model.[3] Clearly, the CI anisotropy is of a remarkable precision.

The polarized spectrum (curve A, Fig. 2) uses the CI trace as input. It is nearly consistent with the result of a rather difficult measurement.[8,9] Curve C is based on previous SCF data.[1] We note that the empirical fit[9] (curve B of Fig. 2) was constrained to also reproduce a second virial dielectric coefficient $B_\epsilon = -0.20$ cm^{6}mol^{-2} consistent with the measurements[13,14]: $B_\epsilon = -0.30 \pm 0.10$ and -0.24 ± 0.04 cm^{6}mol^{-2}. The SCF trace[2] is associated with a $B_\epsilon = -0.14$ cm^{6}mol^{-2}, and the CI contribution[2] reduces this to $B_\epsilon = -0.11$ cm^{6}mol^{-2}. Both values are outside the experimental uncertainties of B_ϵ, but the

spectroscopic measurement is nearly satisfactorily approximated (Fig. 2).

The trace, a numerically very small quantity, is difficult to compute. The CI contributions to the trace must at present be regarded as tentative.[2] The basis extension errors have not been evaluated; they make substantial difference to the SCF values and similar effects must be expected at the CI level. Furthermore, the effects of the higher excitations than those used in the CI calculation may be significant. Nevertheless, the agreement with the spectroscopic measurement is encouraging.

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On the stability criteria of the Kirkwood–Riseman diffusion tensor

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During the last few decades the Kirkwood–Riseman (K.R.) equation has played an important role in the characterization of polymer solutions.[1] However it was found numerically[2] that the preaveraged form of the K.R. diffusion tensor is not positive definite. It is expected that the nonpositive definite property arises solely from a mathematical artifact of the point particle (zero monomer size) assumption rather than something physically realistic.[3] Previously, several authors[4-6] have attempted to remove the singularities via methods other than the one outlined here. On the other hand, for the two sphere diffusion matrix, several exact results can be found in

Happel and Brenner,[7] as well as related treatments by others.[8-11] The purpose of this communication is to provide a simple but convincing proof of the positive definite property of an altered form of the K.R. diffusion tensor by excluding the nonphysical singularities.

The K.R. diffusion tensor is given as[12]

$$\mathbf{D}_{ji} = \mathbf{D}_{ji}^{(1)} + \mathbf{D}_{ji}^{(2)} ; \tag{1}$$

the Stokes law part is given by

$$\mathbf{D}_{ji}^{(1)} = \zeta^{-1} I \delta_{ji} , \tag{1a}$$

where $\zeta = 6\pi\eta a$, η being the solvent viscosity and a the

monomer radius. The second part originates from the hydrodynamic interactions between monomers (Oseen tensor for point particles) as follows:

$$\mathbf{D}_{jl}^{(2)} = \frac{(1-\delta_{jl})}{8\pi\mu R_{jl}} (\mathbf{I} + \hat{R}_{jl}\hat{R}_{jl}) \, , \tag{1b}$$

where, $R_{jl} = R_j - R_l$ is the vector distance of separation between monomers j and l, and $R_{jl} = |R_{jl}|$, $\hat{R}_{jl} = R_{jl}/R_{jl}$. If we look at the following Fourier representation we find:

$$\int_{|\mathbf{k}|<k_c} \frac{d^3k}{(2\pi)^3} e^{-i\mathbf{k}\cdot\mathbf{R}_{jl}} f(k^2)(\mathbf{I} - \hat{k}\hat{k}) = \pi \int_0^{k_c} \frac{dk}{(2\pi)^3} k^2 f(k^2)$$

$$\times \left\{ (\mathbf{I} + \hat{R}_{jl}\hat{R}_{jl}) - (\mathbf{I} - 3\hat{R}_{jl}\hat{R}_{jl}) \frac{d^2}{d(kR_{jl})^2} \left[\frac{\sin(kR_{jl})}{kR_{jl}} \right] \right\} \, , \tag{2}$$

where $\mathbf{I}$ is the unit Cartesian tensor, k is the Fourier space wave vector, $k = |\mathbf{k}|$, and $\hat{k} = \mathbf{k}/k$. If we choose $f(k^2) = (1/\eta k^2)$ and $k_c \to \infty$, Eq. (2) yields the Oseen tensor and therefore the Fourier representation of the Oseen tensor is given by

$$\mathbf{D}_{jl}^{(2)} = (1 - \delta_{jl}) \int_{|\mathbf{k}|<\infty} \frac{d^3k}{(2\pi)^3} e^{-i\mathbf{k}\cdot\mathbf{R}_{jl}} \left(\frac{1}{\eta k^2}\right)(\mathbf{I} - \hat{k}\hat{k}) \, . \tag{1b'}$$

This is the same result as given in Edward and Freed.[13] Here the steady state fluid propagator is $(1/\eta k^2)$ and the transverse projection operator $(\mathbf{I} - \hat{k}\hat{k})$ arises as a consequence of incompressibility ansatz. This is the same result given in Edward and Freed[13] and we refer the interested readers to an excellent review paper by Freed.[14] Next, it is easy to show that the Stokes term $\mathbf{D}_{jl}^{(1)}$ can be represented as

$$\mathbf{D}_{jl}^{(1)} = \delta_{jl} \int_{|\mathbf{k}|<(\pi/2a)} \frac{d^3k}{(2\pi)^3} e^{-i\mathbf{k}\cdot\mathbf{R}_{jl}} \left(\frac{1}{\eta k^2}\right) \, ;$$

note that for $j = l$, $R_{jl} = 0$. This representation invites the following rearrangement:

$$\mathbf{D}_{jl} = \mathbf{D}_{jl}^< + \mathbf{D}_{jl}^> \, , \tag{3}$$

$$\mathbf{D}_{jl}^< = \int_{|\mathbf{k}|<k_c} \frac{d^3k}{(2\pi)^3} e^{-i\mathbf{k}\cdot\mathbf{R}_{jl}} \left(\frac{1}{\eta k^2}\right)(\mathbf{I} - \hat{k}\hat{k}) \, , \tag{3a}$$

$$\mathbf{D}_{jl}^> = (1 - \delta_{jl}) \int_{|\mathbf{k}|>k_c} \frac{d^3k}{(2\pi)^3} e^{-i\mathbf{k}\cdot\mathbf{R}_{jl}} \left(\frac{1}{\eta k^2}\right)(\mathbf{I} - \hat{k}\hat{k}) \, , \tag{3b}$$

where the $\mathbf{D}_{jl}^<$ tensor is the integral term that covers the domain of $k \le k_c = \pi/2a$ and $\mathbf{D}_{jl}^>$ is the term that covers $k \ge k_c$. Physically, one can interprete the subspace of $k \le (\pi/2a)$ as one which provides the real space detail of length scales larger than a, while the subspace $k \ge (\pi/2a)$ provides detail for length scales smaller than a. Furthermore, it can be shown that $\mathbf{D}^<$ is positive definite as follows:

Choose an arbitrary $3N$ dimensional vector $\Phi \equiv (\phi_1, \phi_2, \ldots, \phi_N)$, the ϕ_i's being three dimensional Cartesian vectors. Then

$$\Phi \cdot \mathbf{D}^< \cdot \Phi^{T*} = \int_{|\mathbf{k}|<2\pi/a} \frac{d^3k}{(2\pi)^3}$$

$$\times \sum_j \phi_j e^{i\mathbf{k}\cdot\mathbf{R}_j} \cdot (\mathbf{I} - \hat{k}\hat{k}) \cdot \sum_l \phi_l^* e^{-i\mathbf{k}\cdot\mathbf{R}_l} \, ,$$

$$= \int_{|\mathbf{k}|<k_c} \frac{d^3k}{(2\pi)^3} \Xi(k) \cdot (\mathbf{I} - \hat{k}\hat{k}) \cdot \Xi^*(k) \, ,$$

$$= \int_{|\mathbf{k}|<k_c} \frac{d^3k}{(2\pi)^3} \{|\Xi|^2 - |\Xi \cdot \hat{k}|^2\}^2 \ge 0 \, , \tag{4}$$

where $\Xi = \sum_m \phi_m e^{i\mathbf{k}\cdot\mathbf{R}_m}$.

The above proof illustrates that $\mathbf{D}^<$ is positive definite, and similarly it is easy to show that $\mathbf{D}^>$ is not positive definite by choosing the arbitrary vector Φ appropriately. The interpretation is that length scales of a or less give rise to nonphysical singularities. If one restricts the diffusion tensor to a physically realistic wave vector domain (in other words discarding the unphysical part $\mathbf{D}^>$), one can identify the "optimal positive definite diffusion tensor" ($\mathbf{D}^*$) which is identically $\mathbf{D}^<$. It can also be shown by using Eq. (2) that the preaveraged form of $\mathbf{D}^*$ in real space is the same as that of Fujita[6] and the nonpreaveraged form is structurally similar to the results of Rotne and Prager,[4] and Yamakawa.[5] A comprehensive account of this subject due to Fixman[15] compares computed results with the exact two sphere problem in the nondraining limit.

This stability study could be potentially important for interpreting modern scattering experiments[16] (laser and neutron spin echo) of polymer solutions. The Fourier representation of $\mathbf{D}^*$ (or $\mathbf{D}^<$ as in Eq. (3a)) has appeal as a computational tool, such as nonpreaveraged hydrodynamic interaction used with this adaptation to the positive definite property. The dynamic structure factor for the branched polymers could give 40% error due to preaveraging.[17]

Note also that there may arise physical singularities rather than mathematical singularities mentioned above if one is interested in a high shear rate flow problem. Such an example could be the investigation of the onset of the polymer induced drag reduction.[18] In this case, it is desirable to remove unphysical (mathematical) singularities as reported in the present communication before we study the possible physical singularities.

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Ion mobility test of Li+–Ar potentials

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Recently, Olson and Liu[1] have obtained Li+–Ar potentials using SCF and CI calculations. Both potentials have minima at about 4.5 a.u. with well depths of about 0.01 a.u. (0.27 eV), the SCF well being slightly shallower. These potentials are shown in Fig. 1 together with the potentials of Kim and Gordon,[2] and of Gordon and Waldman,[3] both of which are based on electron gas–Drude model calculations.

Using the ion mobility theory developed by Viehland and Mason,[4,5] the drift velocities v_D of the lithium ions in argon gas may be calculated as a function of E/N, when E is the externally applied electric field and N the neutral gas number density. The reduced mobility K_0 is then given by

$$K_0 = (v_D/N_0)/(E/N) ,$$

where N_0 is the number density at standard temperature and pressure (2.687×10^{19} cm^{-3}). These mobility curves are shown in Fig. 2 for each of the four theoretical potentials. Also shown in Fig. 2 are the experimental mobilities of Akridge, Ellis, Pai, and McDaniel at 300 °K obtained using a drift-tube mass spectrometer.[6] A comparison of the theoretical curves and the data points shows that the GW, KG, SCF, and CI potentials are all reasonable and give progressively better fits to the experimental data. However, there is still a significant difference, particularly at low E/N.

In order to determine where the potential might be adjusted to better fit the mobility data a directly determined potential is developed.[7] This potential (denoted DD) is shown in Fig. 1 and the resulting mobilities,
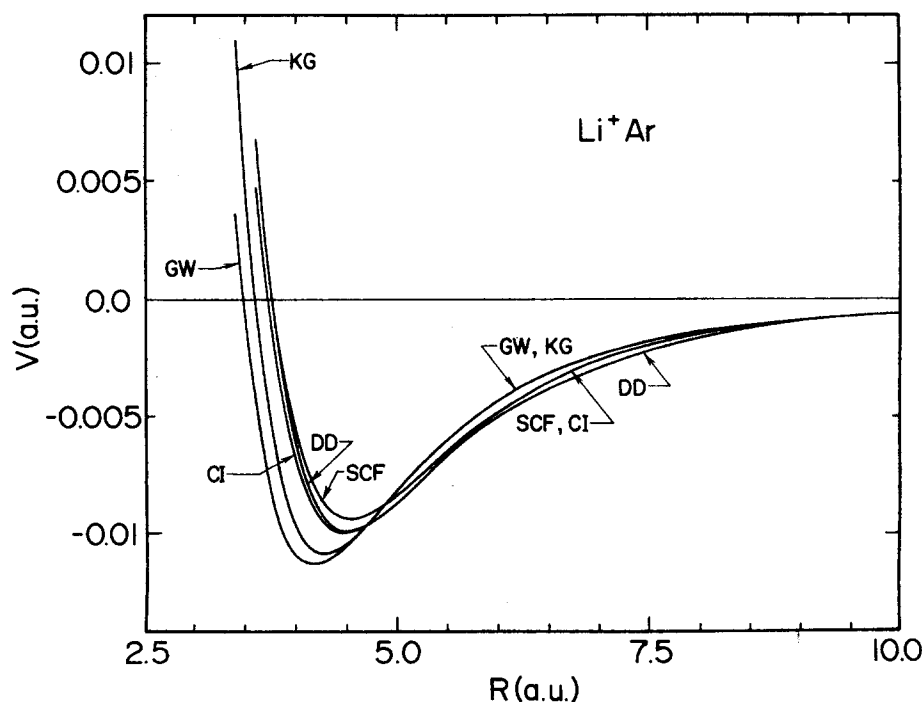

FIG. 1. The Kim–Gordon (KG), Gordon–Waldman (GW), and Olson and Liu SCF and CI theoretical potentials for Li+–Ar, together with the potential (DD) determined directly from the experimental data. Both the internucleus separation distance R and the potential V are in atomic units (0.529177 Å and 27.2116 eV, respectively).