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Note

Angular Monte Carlo Integration Using Quaternion Parameters: A Spherical Reference Potential for CCl_4

The starting point for any perturbation theoretical treatment of molecular liquids is a suitably defined *reference* or *effective* potential $u_{\text{eff}}(r)$. Experience has shown that, in general, for a given anisotropic model potential $u(r, \mathbf{\Omega}_1, \mathbf{\Omega}_2)$, the choice

$$u_{\text{eff}}(r) = -kT \ln b(r), \tag{1a}$$

with

$$b(r) = \frac{1}{\Omega^2} \iint e^{-u(r, \mathbf{\Omega}_1, \mathbf{\Omega}_2)/kT} \, d\mathbf{\Omega}_1 \, d\mathbf{\Omega}_2, \tag{1b}$$

will yield the best results. This means that, at least for the thermodynamic properties, the perturbative terms remain small, and that the pair correlation function $g_{\text{eff}}(r)$ pertaining to $u_{\text{eff}}(r)$ is a good approximation to the centers-pair correlation $g_{00}^{000}(r)$ of the anisotropic particles. (In the linear diatomics case, this latter statement has to be modified [1, 2], but this is irrelevant to what follows.)

In the most general case of nonlinear anisotropic molecules, the double angular integration in (1b) involves 5 variables. Depending on the symmetry of the model molecules, the number of angular variables and the integration regions may be reduced, but that is of no advantage if we want to construct a generally applicable computer program. Very often, straightforward angular step integration is used to evaluate (1b). In this case, the influence of the angular step size must be assessed carefully, since the integrand may vary rather sharply with the angle variables. The use of a Romberg integration scheme may be of advantage in this respect, but such schemes tend to be time-consuming when applied to multidimensional problems. An attractive alternative is the simple Monte Carlo integration. For a given pair distance r, a sequence of K random orientational configurations $(\mathbf{\Omega}_1, \mathbf{\Omega}_2)$ with energies u_k $(k = 1, \ldots, K)$ is sampled. An unbiased estimate b^{MC} of $b(r)$ is then given by

$$b^{\text{MC}} = \frac{1}{K} \sum_{k=1}^{K} e^{-u_k/kT}. \tag{2a}$$

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The standard error of b^{MC} is

$$(\delta b^{\mathrm{MC}})^2 = \frac{1}{K-1}\left[\frac{1}{K}\sum_{k=1}^{K} e^{-2u_k/kT} - (b^{\mathrm{MC}})^2\right]. \tag{2b}$$

When evaluating (2a), it is advantageous to avoid the use of Euler angles, since in most machines the computation of trigonometric functions is lengthy. Moreover, the potential $u(r, \mathbf{\Omega}_1, \mathbf{\Omega}_2)$ figuring in the integrand is not as a rule given explicitly in terms of angles, but rather of site-site distances, as in the case of n-Lennard–Jones-centers models which are defined by

$$u(r, \mathbf{\Omega}_1, \mathbf{\Omega}_2) = \sum_{i=1}^{n}\sum_{j=1}^{n} u^{\mathrm{LJ}}(r_{ij}), \tag{3}$$

where i and j denumerate the LJ centers in each of the two interacting molecules. The introduction of Euler angles is therefore quite unnecessary in the first place. We shall use the symmetric quaternion parameters instead [3, 4], taking advantage of a sampling method due to Marsaglia. It will be shown that whenever orientations have to be picked at random, replacement of Euler angles by quaternion parameters will save computing time. Details of the method given below may therefore be of advantage also in the more general case of of Metropolis-type Monte Carlo calculations on systems of structured molecules (see, e.g., [5] and references quoted therein). As a rule, however, the subsequent evaluation of $N(N-1)/2$ pair interactions is the most time-consuming step in such calculations, so that the speeding-up of the orientation sampling is of minor importance there.

For clarity, the simple case of linear molecules will be considered first. The orientation of such a particle is defined most simply in terms of the three Cartesian components of a unit vector. The presence of one unnecessary parameter [3 instead of 2 orientational coordinates) is more than offset by the formal symmetry and the absence of trigonometric functions. Randomly oriented unit vectors are most efficiently sampled using a technique due to Marsaglia [6]. This procedure consists of the following two steps:

(a) generate pairs of random numbers ξ_1, ξ_2 independent and uniform on the interval $(-1, 1)$ until $S = \xi_1^2 + \xi_2^2 < 1$;

(b) form the random unit vector

$$\{e_x, e_y, e_z\} = \{2\xi_1\sqrt{1-S}, 2\xi_2\sqrt{1-S}, 1-2S\}.$$

For nonlinear bodies, the four quaternion parameters serve the same purpose as the three Cartesian unit vector components in the linear case. A random orientation may now be characterized by a set of parameters $\mathbf{\Lambda} = \{\lambda, \mu, \nu, \rho\}$ which fulfill the sole condition $\lambda^2 + \mu^2 + \nu^2 + \rho^2 = 1$ (analogous to the condition $e_x^2 + e_y^2 + e_z^2 = 1$ for a random unit vector). But this is a tantamount to saying that we have to pick the vector $\mathbf{\Lambda}$ at random on the surface of a four-dimensional unit sphere. Again, Marsaglia [6] has given a prescription for doing this in a fast and efficient manner:

(a) generate pairs of random numbers ξ_1, ξ_2 independent and uniform on $(-1, 1)$ until $S_1 = \xi_1^2 + \xi_2^2 < 1$;

(b) do the same for pairs ξ_3, ξ_4 until $S_2 = \xi_3^2 + \xi_4^2 < 1$;

(c) form the random unit 4-vector

$$\mathbf{\Lambda} = \{\xi_1, \xi_2, \xi_3 \sqrt{(1 - S_1)/S_2}, \xi_4 \sqrt{(1 - S_1)/S_2}\}.$$

On a CDC 170–720 the average computing tume for the cycle a through c is 1.36×10^{-4} sec. The equivalent task of picking a random orientation using Euler angles takes 5.51×10^{-4} sec. on the average.

For a given distance r, a large number (2×10^3 to 1×10^4) of random orientations $\mathbf{\Omega}_1, \mathbf{\Omega}_2$ of the two molecules is sampled in this way. Having picked a particular orientational pair configuration, we want to calculate the potential energy given by Eq. (3). To do this, we need the position vectors $\mathbf{r}_L$, in the laboratory frame, of all interaction sites in the two molecules. The vectors $\mathbf{r}_L$ may be calculated from the intramolecular position vectors $\mathbf{r}_M$ by

$$\mathbf{r}_L = \overleftrightarrow{A} \cdot \mathbf{r}_M, \tag{4a}$$

where the rotation matrix is trivial in the linear case, and in the nonlinear case has the form [3]

$$\overleftrightarrow{A} = \begin{pmatrix} \lambda^2 - \mu^2 - \nu^2 + \rho^2 & 2(\lambda\mu - \nu\rho) & 2(\nu\lambda + \mu\rho) \\ 2(\lambda\mu + \nu\rho) & \mu^2 - \nu^2 - \lambda^2 + \rho^2 & 2(\mu\nu - \lambda\rho) \\ 2(\nu\lambda - \mu\rho) & 2(\mu\nu + \lambda\rho) & \nu^2 - \lambda^2 - \mu^2 + \rho^2 \end{pmatrix}. \tag{4b}$$

It should be noted at this point that it is quite easy to include fractional charges (in addition to the LJ interaction sites) in this scheme, thus mimicking the action of molecular multipoles.

Application to CCl_4. In order to give a specific example we have applied the method to a tetrahedral 4-LJ model of CCl_4. The parameters of this model, as used by Steinhauser and Neumann (SN) in a molecular dynamics study [7], are $\varepsilon_0/k = 120K$, $\sigma_0 = 3.4$Å and $l = 1.77$Å (C–Cl bond length). We have calculated the effective potential for this system at ten temperatures between 210 K and 1365 K. By comparing the resulting second virial coefficient $B_2(T)$ with experimental data [9], we conclude that the well depth ε_0 of the Cl-Cl interaction should be $\varepsilon_0 = 210k$ instead of $120k$. The effective potential calculated with this improved ε_0 is depicted in Fig. 1. It turns out that the repulsive part of $u_{\text{eff}}(r)$ may be approximated very well by a Kihara potential defined as

$$u_{\text{Kih}}(r) = 4\varepsilon \left[\left(\frac{r - a}{\sigma - a} \right)^{-12} - \left(\frac{r - a}{\sigma - a} \right)^{-6} \right], \tag{12a}$$

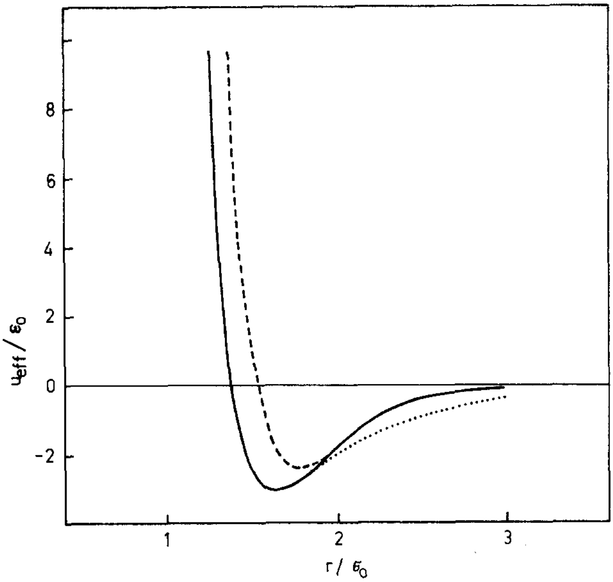

FIG. 1. Reference potential of CCl_4 at two temperatures: (—), $T = 315$ K; (– – –), $T = 840$ K; (···), Kihara approximation (Eq. 6) to $u_{eff}(r)$ at the lower temperature.

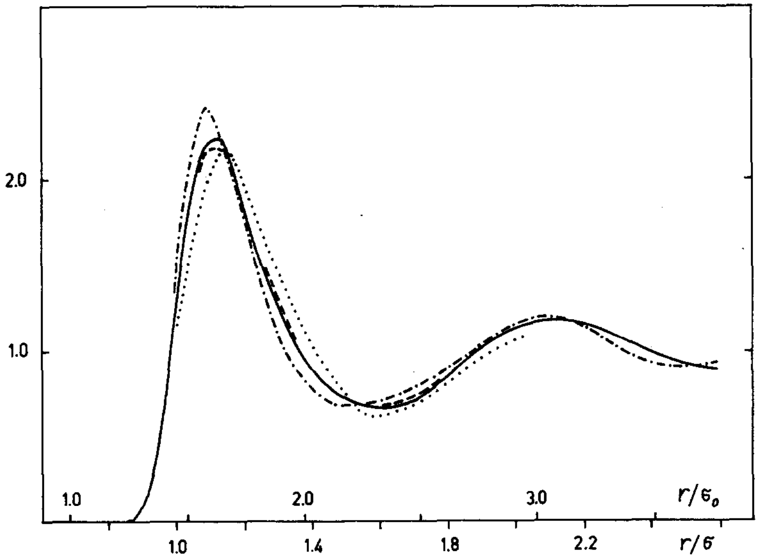

FIG. 2. Pair correlation function pertaining to $u_{eff}(r)$ at $\rho = 6.24 \cdot 10^{-3}$ Å^{-3} and $T = 300$ K. (—), $g_{eff}(r)$ from simulation with $u_{eff}(r)$; (– – –), $g_{Kih}(r)$ from simulation with $u_{Kih}(r)$ instead of $u_{eff}(r)$: (···), $g_{00}^{000}(r)$ from full MD simulation by Steinhauser *et al.* [7]; (– · –), Percus–Yevick pair correlation function to $u_{eff}(r)$.

TABLE I

	$\varepsilon^* = \varepsilon/\varepsilon_0$	$\sigma^* = \sigma/\sigma_0$	$d^* = d/\sigma_0$
a_0	5.08250	1.21990	1.27040
a_1	−2.14940	0.11068	0.41717
a_2	0.67544	−0.00039	−0.14939
a_3	−0.09928	−0.00292	0.02589
a_4	0.00551	0.00027	0.00164

Note. Polynomial fit to the Kihara parameters of the reference potential for CCl_4 (see Eq. 6). In the range $1 \leqslant T^* \leqslant 6.5$, the fit is better than 1.5% for ε^* and $\leqslant 0.5\%$ for σ^* and d^*. The data to be fitted had r.m.s. errors of 0.5% (ε^*), 0.2% (σ^*), and 1% (d^*).

where the Kihara parameter a may be extracted from the distance of zero force d using

$$a = (d - \sqrt[6]{2}\sigma)/(1 - \sqrt[6]{2}). \tag{12b}$$

Beyond the potential minimum, the Kihara function deviates from $u_{\mathrm{eff}}(r)$. It is the repulsive part, however, which dominates the structure of a model system at liquid densities. This is illustrated by Fig. 2, which shows the pair correlation functions pertaining to $u_{\mathrm{eff}}(r)$ and $u_{\mathrm{Kih}}(r)$ at $\rho = 6.24 \times 10^{-3}$ Å^{-3} and $T = 300$ K. The functions $g_{\mathrm{eff}}(r)$ and $g_{\mathrm{Kih}}(r)$ were computed by short MD runs using $u_{\mathrm{eff}}(r)$ and $u_{\mathrm{Kih}}(r)$, respectively. Also shown in Fig. 2 is the centers pair correlation function $g_{00}^{000}(r)$ given by SN, and finally, $g_{\mathrm{PY}}(r)$ as predicted by Percus–Yevick theory (applied to $u_{\mathrm{eff}}(r)$).

In view of the good agreement between $g_{\mathrm{Kih}}(r)$ and $g_{\mathrm{eff}}(r)$, it seems worthwhile to consider the Kihara approximation the the effective potential more closely. In particular, the reduced Kihara parameters $\varepsilon^* = \varepsilon/\varepsilon_0$, $\sigma^* = \sigma/\sigma_0$, and $d^* = d/\sigma_0$ as functions of the reduced temperature $T^* = kT/\varepsilon_0$ may be represented by least squares polynomials in T^*. The coefficients of these polynomials are listed in Table I.

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