Orthogonal polynomial approach to fluids with internal degrees of freedom: The case of polar, polarizable molecules

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The molecules of real liquids have internal degrees of freedom that may couple with the external coordinates of position and orientation so that they affect and are affected by the microscopic liquid structure. For cases where the internal coordinates possess a Boltzmann-like distribution, a procedure was recently proposed [Phys. Rev. E **55**, 426 (1997)] whereby the internal coordinates are incorporated into the conventional integral equation formulation of classical liquid state theory with no approximations beyond some reliable closure relation familiar from simple liquids. The basis of the procedure is expansions in special orthogonal polynomials of the internal coordinates. Here we use this technique to obtain the structural, thermodynamic, and electrostatic properties of a classical liquid of polar polarizable molecules, with classical Drude oscillators modeling the internal variable of fluctuating polarization. Sample results obtained using several approximate closures are compared with simulation data. © *1998 American Institute of Physics.* [S0021-9606(98)50711-8]

I. INTRODUCTION

Atoms and molecules have internal structure whose changes could alter the effective pair potentials that couple them to other neighboring atoms and molecules and thereby rearrange their external environment in a condensed state. Conversely, geometrical rearrangement of the neighbors of an atom or molecule could, through the same interactions, change its internal structure. In most instances, the thermal energies of these external structural rearrangements are insufficient to excite internal quantum degrees of freedom and so atoms and molecules are for practical purposes inert entities in most calculations of the microscopic structure of condensed materials. However, some changes of internal structure involving relatively large masses, such as individual atoms in a polyatomic molecule (leading to fluctuations in bond lengths and angles) or the electronic center of mass and the atomic nucleus (leading to fluctuations in the electric dipole moment), may be accessible to ambient thermal energies. In such cases, a careful calculation of the microscopic geometrical structure of the condensed state would need to take into account these internal degrees of freedom. With Monte Carlo or molecular dynamics simulation this is in fact readily done (at least in the classical limit) simply by generalizing the Hamiltonian that governs the calculations, the simulation algorithms being otherwise unchanged.[1,2] Theoretical methods are more specifically tailored and the desired inclusion of internal degrees of freedom entails a corresponding generalization of the theoretical methods themselves. Such a generalization was recently proposed by one of us to study classical liquids with internal degrees of freedom and applied specifically to liquids of nonpolar polarizable atoms.[3] In this paper we extend this integral equation technique to the case of *polar* polarizable atoms.

Polarization as an internal degree of freedom coupled to the external center-of-mass coordinates through dipole–dipole forces was introduced into liquid-state calculations by Høye and Stell[4] and Pratt,[5] who studied this model in mean spherical approximation (MSA). We follow these authors in assuming that in the gas phase the instantaneous dipole moment $\mathbf{p}$ of an atom fluctuates randomly with an intrinsic thermal distribution of Gaussian form,

$$f_0(p)=\frac{1}{(2\pi\alpha_0/\beta)^{3/2}}\exp\left(-\frac{\beta p^2}{2\alpha_0}\right), \tag{1}$$

where α_0 is the atomic polarizability and $\beta=1/k_BT$, with T the Kelvin temperature and k_B Boltzmann's constant. The properties of a fluid of N such polarizable atoms in a volume V, interacting pairwise through a potential $u_0(r)$ and having no permanent polarization, are then obtained from the canonical partition function,

$$Z=\frac{1}{V^N}\int\prod_{j=1}^{N}[d\mathbf{r}_j d\mathbf{p}_j f_0(p_j)] \times\exp\left(-\beta\sum_{i<j}[u_0(r_{ij})+u_{dd}(\mathbf{r}_{ij},\mathbf{p}_i,\mathbf{p}_j)]\right). \tag{2}$$

Here u_{dd} is the dipole–dipole potential,

$$u_{dd}(\mathbf{r},\mathbf{p}_1,\mathbf{p}_2)=-\frac{1}{r^3}[3(\hat{\mathbf{r}}\cdot\mathbf{p}_1)(\hat{\mathbf{r}}\cdot\mathbf{p}_2)-\mathbf{p}_1\cdot\mathbf{p}_2], \tag{3}$$

where $\hat{\mathbf{r}}$ is the unit vector in the $\mathbf{r}$ direction, while for u_0 we choose the Lennard-Jones potential,

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$$u_0(r)=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]. \tag{4}$$

This is the model studied in Ref. 3. The key quantities needed for a complete thermodynamic and electrostatic description of this system are the one-body and two-body distribution functions,

$$\rho^{(1)}(\mathbf{r},\mathbf{p})=\left\langle \sum_{j=1}^{N}\delta(\mathbf{r}-\mathbf{r}_j)\,\delta(\mathbf{p}-\mathbf{p}_j)\right\rangle=\rho f(p), \tag{5}$$

$$\begin{aligned}\rho^{(2)}&(\mathbf{r},\mathbf{p},\mathbf{r}',\mathbf{p}')\\&=\left\langle \sum_{i\neq j}\delta(\mathbf{r}-\mathbf{r}_i)\,\delta(\mathbf{p}-\mathbf{p}_i)\,\delta(\mathbf{r}'-\mathbf{r}_j)\,\delta(\mathbf{p}'-\mathbf{p}_j)\right\rangle\\&=\rho^2 f(p)f(p')g(\mathbf{r}-\mathbf{r}',\mathbf{p},\mathbf{p}'),\end{aligned} \tag{6}$$

where $\rho=N/V$ is the density and $f(p)$ the new shape taken on in the dense liquid by the original gas-phase distribution $f_0(p)$. Coupled equations for these distribution functions are readily obtained within the Ornstein–Zernike formalism. The practical problem then encountered is that quantities such as the pair distribution function $g(\mathbf{r},\mathbf{p}_1,\mathbf{p}_2)$ depend on six independent variables and are not realistically manageable in numerical solutions. The approach developed in Ref. 3 is simply to extend the familiar practice[6,7] of expansion in spherical harmonics $Y_{lm}(\omega)$, breaking out the dependence on the orientations ω_1,ω_2 of the vectors $\mathbf{p}_1,\mathbf{p}_2$, to an additional expansion in polynomials $Q_{nl}(p)$, breaking out as well the dependence on the new internal variables, the fluctuating dipole moments p_1,p_2. Thus, $g(\mathbf{r},\mathbf{p}_1,\mathbf{p}_2)$ for example is written in expanded form as

$$\begin{aligned}g(\mathbf{r},\mathbf{p}_1,\mathbf{p}_2)=4\pi&\sum_{n_1,n_2,l_1,l_2,m} g^{n_1n_2}_{l_1l_2m}(r)Q_{n_1l_1}(p_1)Q_{n_2l_2}(p_2)\\&\times Y_{l_1m}(\omega_1)Y_{l_2\bar{m}}(\omega_2),\end{aligned} \tag{7}$$

where the Euler angles $\omega=(\theta,\phi)$ are defined with the z axis along $\mathbf{r}$ and the summation indices satisfy the constraints[8]

$$\begin{aligned}&n=0,1,2,3,\ldots,\\&l=n,n-2,n-4,\ldots,1\ \text{or}\ 0,\\&m=0,\pm1,\pm2,\ldots,\pm l.\end{aligned} \tag{8}$$

The defining characteristic of the polynomials $Q_{nl}(p)$ is that they are orthonormal with weight function $f(p)$,

$$4\pi\int_0^\infty dp\,p^2 f(p)Q_{nl}(p)Q_{n'l}(p)=\delta_{nn'}. \tag{9}$$

For a Gaussian $f(p)$, the $Q_{nl}(p)$ are the eigenfunctions of the three-dimensional harmonic oscillator in spherical coordinates.[3,8]

In the next section, we add to these basic ingredients a permanent dipole moment $\boldsymbol{\mu}_0$ on each atom, so that the total moment $\mathbf{m}=\boldsymbol{\mu}_0+\mathbf{p}$ now also fluctuates in magnitude and direction. This leads to a new distribution function $F_0(m)$ and so to new polynomials $Q_{nl}(m)$, but otherwise precisely the same algorithm is employed to study polar polarizable systems as was used earlier for the nonpolar case. A brief summary of this algorithm is included in Section II, while sample numerical results are given in Section III and compared there with simulation data.

II. INTEGRAL EQUATION THEORY FOR POLAR POLARIZABLE MOLECULES

Assigning to each atom a permanent dipole moment $\boldsymbol{\mu}_0$ in addition to its fluctuating moment $\mathbf{p}$ introduces for each atom two new degrees of freedom, the Euler angles ω_0 for the direction of $\boldsymbol{\mu}_0$. The partition function for a system of polar polarizable atoms is then

$$\begin{aligned}Z=\frac{1}{(4\pi V)^N}\int\prod_{j=1}^{N}&[d\mathbf{r}_j d\mathbf{p}_j d\omega_{0j}f_0(p_j)]\\&\times\exp\left(-\beta\sum_{i<j}[u_0(r_{ij})+u_{dd}(\mathbf{r}_{ij},\mathbf{m}_i,\mathbf{m}_j)]\right),\end{aligned} \tag{10}$$

where now the dipolar interactions depend on the total moments $\mathbf{m}_j=\boldsymbol{\mu}_{0j}+\mathbf{p}_j$. We can simplify this expression with the operations

$$\begin{aligned}\frac{1}{4\pi}\int d\mathbf{p}\,d\omega_0 f_0(p)(\cdots)&=\frac{1}{4\pi}\int d\mathbf{m}\,d\omega_0 f_0(|\mathbf{m}-\boldsymbol{\mu}_0|)(\cdots)\\&=\int d\mathbf{m}F_0(m)(\cdots),\end{aligned} \tag{11}$$

where

$$F_0(m)\equiv\frac{1}{4\pi}\int d\omega_0\,\frac{\exp[-\beta(\mathbf{m}-\boldsymbol{\mu}_0)^2/2\alpha_0]}{(2\pi\alpha_0/\beta)^{3/2}}. \tag{12}$$

Putting the z axis along $\mathbf{m}$, we easily find

$$F_0(m)=\frac{\exp[-\beta(m^2+\mu_0^2)/2\alpha_0]}{(2\pi\alpha_0/\beta)^{3/2}}\,\frac{\sinh(\beta\mu_0 m/\alpha_0)}{\beta\mu_0 m/\alpha_0}. \tag{13}$$

The partition function for polar polarizable molecules now becomes

$$\begin{aligned}Z=\frac{1}{V^N}\int\prod_{j=1}^{N}&[d\mathbf{r}_j d\mathbf{m}_j F_0(m_j)]\\&\times\exp\left(-\beta\sum_{i<j}[u_0(r_{ij})+u_{dd}(\mathbf{r}_{ij},\mathbf{m}_i,\mathbf{m}_j)]\right).\end{aligned} \tag{14}$$

Comparison with Eq. (2) shows that with the substitution

$$\mathbf{p},f_0(p)\rightarrow\mathbf{m},F_0(m),$$

this is the *same calculation* as that of nonpolar polarizable molecules and can be solved with the same algorithm. Only the numerical coefficients in the polynomials $Q_{nl}(m)$ will be different.

In the limit of vanishing μ_0, $F_0(m)$ obviously reduces to $f_0(p)$, as expected; less obviously, but again as expected, in the limit of vanishing polarizability the distribution function $F_0(m)$ becomes

$$\lim_{\alpha_0\rightarrow0}F_0(m)=\frac{\delta(m-\mu_0)}{4\pi m^2}, \tag{15}$$

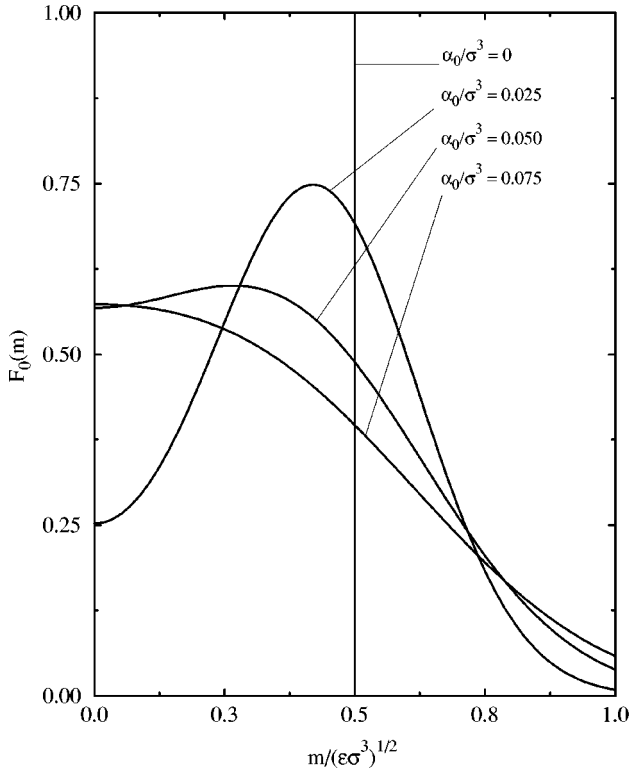

FIG. 1. Distribution function $F_0(m)$ of the total dipole moment m with permanent moment $\mu_0/(\varepsilon\sigma^3)^{1/2} = 0.50$ and temperature $k_BT/\varepsilon = 1.35$, for several polarizabilities α_0. The vertical line at $m/(\varepsilon\sigma^3)^{1/2} = 0.50$ symbolizes a Dirac delta function.

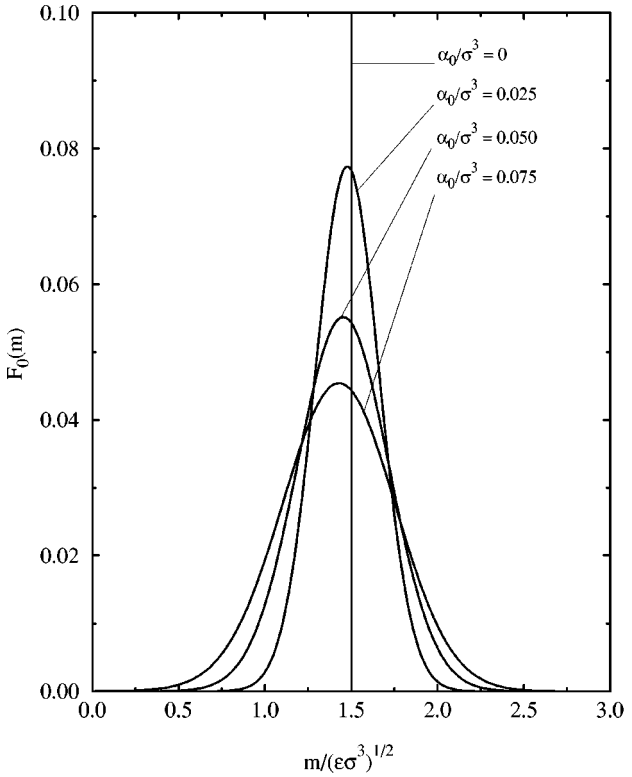

FIG. 2. Distribution function $F_0(m)$ of the total dipole moment m with permanent moment $\mu_0/(\varepsilon\sigma^3)^{1/2} = 1.50$ and temperature $k_BT/\varepsilon = 1.35$, for several polarizabilities α_0. The vertical line at $m/(\varepsilon\sigma^3)^{1/2} = 1.50$ symbolizes a Dirac delta function.

which describes dipoles of fixed length μ_0, or permanent dipoles. The shape of $F_0(m)$ for several values of α_0 and μ_0 is shown in Figures 1 and 2. Since $F_0(m)$ with finite μ_0 is not a classical weight function, the $Q_{nl}(m)$ are constructed explicitly using Gram–Schmidt orthogonalization.[9,10] For this one needs the moments $\langle m^{2j}\rangle$ of $F_0(m)$, which are found in Appendix A.

As earlier in the nonpolar case, the complete thermodynamic and electrostatic properties of the polar system are obtainable from the dipole distribution function $F(m)$ and the generalized pair distribution function $g(\mathbf{r},\mathbf{m},\mathbf{m}')$, defined as in Eqs. (5) and (6) with $\mathbf{m}$ replacing $\mathbf{p}$. The two distribution functions are coupled by the intermolecular potential u_{dd}. A direct expression of this coupling is obtained by differentiating $F(m)$ to yield

$$\frac{d}{dm}\ln\left[\frac{F(m)}{F_0(m)}\right] = -\rho\int d\mathbf{r}d\mathbf{m}'F(m') \times g(\mathbf{r},\mathbf{m},\mathbf{m}')\beta u_{dd}(\mathbf{r},\hat{\mathbf{m}},\mathbf{m}'), \tag{16}$$

the first member of a Kirkwood–Born–Green–Yvon hierarchy.[11] The calculation of $F(m)$ from this equation requires knowing g. In classical liquid state theory, the pair distribution function is obtained from the Ornstein–Zernike (OZ) equation and a closure relation.[12] The first of these, generalized for fluctuating dipoles, reads as

$$h(\mathbf{r}_{12},\mathbf{m}_1,\mathbf{m}_2) = c(\mathbf{r}_{12},\mathbf{m}_1,\mathbf{m}_2) + \rho\int d\mathbf{r}_3 d\mathbf{m}_3 F(m_3) \times h(\mathbf{r}_{13},\mathbf{m}_1,\mathbf{m}_3)c(\mathbf{r}_{32},\mathbf{m}_3,\mathbf{m}_2), \tag{17}$$

where $h = g - 1$ and c is the direct correlation function. The second, or closure, relation expresses c back in terms of g and the system's interactions,

$$c(\mathbf{r},\mathbf{m}_1,\mathbf{m}_2) = -\beta u_0(r) - \beta u_{dd}(\mathbf{r},\mathbf{m}_1,\mathbf{m}_2) + h(\mathbf{r},\mathbf{m}_1,\mathbf{m}_2) - \ln[1 + h(\mathbf{r},\mathbf{m}_1,\mathbf{m}_2)] + B(\mathbf{r},\mathbf{m}_1,\mathbf{m}_2). \tag{18}$$

This relation must be supplemented with an approximation for B, the so-called bridge function, which is formally defined in terms of a diagram summation that offers little practical benefit.

The iterative solution of these equations follows that of the earlier nonpolar case.[3] Starting the iterations with $F(m) = F_0(m)$, one constructs the polynomials $Q_{nl}(m)$ as described in Appendix B. The (OZ+closure) equations are then solved for the coefficients $\gamma^{n_1 n_2}_{l_1 l_2 m}(r)$ of $\gamma = h - c$ in an iterated loop

(1) *Closure relation + Fourier transform:*

$$\gamma(\mathbf{r},\mathbf{m}_1,\mathbf{m}_2)=4\pi\sum_{n_1,n_2,l_1,l_2,m}\gamma^{n_1n_2}_{l_1l_2m}(r)\times Q_{n_1l_1}(m_1)Q_{n_2l_2}(m_2)\times Y_{l_1m}(\omega_1)Y_{l_2\bar{m}}(\omega_2), \tag{19}$$

$$c(\mathbf{r},\mathbf{m}_1,\mathbf{m}_2)=\exp[-\beta u_0(r)-\beta u_{dd}(\mathbf{r},\mathbf{m}_1,\mathbf{m}_2)+\gamma(\mathbf{r},\mathbf{m}_1,\mathbf{m}_2)+B(\mathbf{r},\mathbf{m}_1,\mathbf{m}_2)]-1-\gamma(\mathbf{r},\mathbf{m}_1,\mathbf{m}_2), \tag{20}$$

$$c^{n_1n_2}_{l_1l_2m}(r)=4\pi\int d\mathbf{m}_1 d\mathbf{m}_2 F(m_1)F(m_2)\times c(\mathbf{r},\mathbf{m}_1,\mathbf{m}_2)Q_{n_1l_1}(m_1)Q_{n_2l_2}(m_2)\times Y^*_{l_1m}(\omega_1)Y^*_{l_2\bar{m}}(\omega_2), \tag{21}$$

$$c^{n_1n_2}_{l_1l_2m}(r)\rightarrow\tilde{c}^{n_1n_2}_{l_1l_2m}(k). \tag{22}$$

(2) *OZ equation + inverse Fourier transform:*

$$\tilde{\gamma}^{n_1n_2}_{l_1l_2m}(k)=(-1)^m\rho\sum_{n_3,l_3}[\tilde{\gamma}^{n_1n_3}_{l_1l_3m}(k)+\tilde{c}^{n_1n_3}_{l_1l_3m}(k)]\times\tilde{c}^{n_3n_2}_{l_3l_2m}(k), \tag{23}$$

$$\tilde{\gamma}^{n_1n_2}_{l_1l_2m}(k)\rightarrow\gamma^{n_1n_2}_{l_1l_2m}(r). \tag{24}$$

The sums in (19) and (21) (the latter as discrete Gaussian quadratures; see Appendix C) constitute separable, five-dimensional transforms. They are each executed as five successive one-dimensional transforms, following a generalized fast-transform algorithm proposed by Orszag.[13] Because the angles ω associated with the conjugate coefficients are defined in different spaces (with the z axis along $\mathbf{r}$ in one case and along $\mathbf{k}$ in the other) there are several parts to the Fourier transforms in (22) and (24) that are detailed in earlier publications.[14,15]

With a converged solution of the (OZ+closure) equations in hand, one turns to Eq. (16) to recalculate $F(m)$. In expanded form, this equation reads as

$$\frac{d}{dm}\ln\left[\frac{F(m)}{F_0(m)}\right]=-\frac{2}{\langle m^2\rangle^{1/2}}\sum_{n=2,4,6,\ldots}\xi_n Q_{n-1,1}(m), \tag{25}$$

where

$$\xi_n=\tfrac{1}{2}\rho\int d\mathbf{r}\sum_{m=-1,0,1}g^{n-1,1}_{11m}(r)\beta u^{11}_{11\bar{m}}(r). \tag{26}$$

For the cases studied in the next section, it turns out that the first term of the sum in Eq. (25) is by far the dominant contribution; retaining just this term, we integrate to get

$$\ln\left[\frac{F(m)}{F_0(m)}\right]\approx\left(1-\frac{m^2}{\langle m^2\rangle}\right)\xi_2+C, \tag{27}$$

$$\ln F(m)\approx-\frac{3}{2}\ln\left(2\pi\frac{\alpha_0}{\beta}\right)+\ln\left[\frac{\sinh(\beta\mu_0 m/\alpha_0)}{\beta\mu_0 m/\alpha_0}\right]-\frac{\beta}{2\alpha_0}(m^2+\mu_0^2)+\left(1-\frac{m^2}{\langle m^2\rangle}\right)\xi_2+C, \tag{28}$$

where C is an arbitrary constant fixed by normalization. Now put

$$\alpha=a\alpha_0,\quad \mu=a\mu_0, \tag{29}$$

with

$$a=\frac{1}{1+2\alpha_0\xi_2/\beta\langle m^2\rangle}. \tag{30}$$

One can then show that

$$\ln F(m)\approx-\frac{3}{2}\ln\left(2\pi\frac{\alpha}{\beta}\right)+\ln\left[\frac{\sinh(\beta\mu m/\alpha)}{\beta\mu m/\alpha}\right]-\frac{\beta}{2\alpha}(m^2+\mu^2). \tag{31}$$

That is, the new distribution $F(m)$ will have the *same form* as $F_0(m)$ but with α_0,μ_0 replaced by α,μ. The moments $\langle m^{2j}\rangle$ and the coefficients of u_{dd} will reflect these changes. Specifically, we have from Appendix A

$$\langle m^2\rangle=\mu^2+3\alpha k_BT=a^2\mu_0^2+3a\alpha_0k_BT, \tag{32}$$

while the coefficients of u_{dd} are

$$u^{11}_{110}(r)=-\frac{2}{3}\frac{\langle m^2\rangle}{r^3}, \tag{33}$$

$$u^{11}_{111}(r)=u^{11}_{11-1}(r)=-\frac{1}{3}\frac{\langle m^2\rangle}{r^3}. \tag{34}$$

The (OZ+closure) equations are now solved again with these new dipole–dipole coefficients and the result used to calculate $F(m)$ once more. This process is repeated until self-consistent values are found both for $F(m)$ and for the pair functions.

The recalculation formula for α and μ described above is precisely that developed in Wertheim's renormalized 1-R theory,[16] Høye and Stell's MSA solution,[4] and Carnie and Patey's self-consistent mean field.[17] The numerical values obtained here will in general be different, however, since other closures can now be used.

As noted earlier, the correlation function coefficients completely describe the thermodynamic and electrostatic properties of the polarizable liquid. In particular, we recall that its dielectric constant ϵ is neatly expressed as[3]

$$\epsilon=\frac{1-\rho\tilde{h}^{11}_{111}(0)}{1+\rho\tilde{h}^{11}_{110}(0)}, \tag{35}$$

TABLE I. Computed thermodynamic and electrostatic properties of a polar polarizable Lennard-Jones fluid for $\rho\sigma^3 = 0.80$ and $k_BT/\varepsilon = 1.35$. Molecular dynamics data are from Pollock, Alder, and Patey (Ref. 23). The simulation uncertainties in the last digit of ϵ are given in parentheses.

$\mu_0/(\varepsilon\sigma^3)^{1/2}$	α_0/σ^3		$U_0/N\varepsilon$	$U_{dd}/N\varepsilon$	$\beta p/\rho$	ξ_2	ξ_4	$\mu/(\varepsilon\sigma^3)^{1/2}$	α/σ^3	$m_e/(\varepsilon\sigma^3)^{1/2}$	ϵ
0.50	0	MD	−5.20	−0.083				0.50			1.78(4)
		RHNC	−5.249	−0.077	2.347	0	0	0.50	0	0.50	1.75
		HNC	−4.950	−0.080	3.846	0	0	0.50	0	0.50	1.75
		SSC	−4.954	−0.080	3.829	0	0	0.50	0	0.50	1.75
0.50	0.050	MD	−5.19	−0.22				0.53			2.79(4)
		RHNC	−5.241	−0.263	2.247	−0.1949	0.0007	0.528	0.0528	0.702	2.76
		HNC	−4.942	−0.275	3.744	−0.2034	0.0009	0.529	0.0529	0.703	2.76
		SSC	−4.954	−0.277	3.683	−0.2049	0	0.530	0.0530	0.704	2.78
0.50	0.075	MD	−5.15	−0.30				0.57			3.41(7)
		RHNC	−5.233	−0.415	2.177	−0.3073	0.0021	0.554	0.0830	0.802	3.52
		HNC	−4.935	−0.436	3.661	−0.3227	0.0028	0.556	0.0834	0.804	3.53
		SSC	−4.954	−0.440	3.563	−0.3258	0	0.557	0.0835	0.805	3.58
1.50	0	MD	−5.01	−2.95				1.50			21(1)
		RHNC	−5.078	−2.836	1.125	0	0	1.50	0	1.50	20.5
		HNC	−4.783	−2.937	2.537	0	0	1.50	0	1.50	20.0
		SSC	−4.954	−3.017	1.654	0	0	1.50	0	1.50	26.1
1.50	0.025	MD	−4.99	−3.44				1.62			31(2)
		RHNC	−4.986	−3.767	0.854	−2.7902		1.612	0.0269	1.646	31.5
		HNC	−4.687	−3.946	2.220	−2.9227		1.617	0.0270	1.651	32.7
		SSC	−4.954	−3.943	0.968	−2.9204	0	1.617	0.0270	1.650	44.1

where the superscripts 11 reflect the fact that the potential u_{dd} is bilinear in the dipole moments. Alternatively, ϵ can be found from[3]

$$\frac{(\epsilon-1)(2\epsilon+1)}{3\epsilon} = \frac{4}{3}\pi\beta\langle m^2\rangle\rho\left[1+\frac{1}{3}\rho\tilde{h}^{11}_{\Delta}(0)\right], \tag{36}$$

$$\frac{(\epsilon-1)^2}{\epsilon} = -\frac{4}{3}\pi\beta\langle m^2\rangle\rho^2\tilde{h}^{11}_{D}(0), \tag{37}$$

where

$$\tilde{h}^{11}_{\Delta}(k) \equiv \tilde{h}^{11}_{110}(k) - 2\tilde{h}^{11}_{111}(k), \tag{38}$$

$$\tilde{h}^{11}_{D}(k) \equiv \tilde{h}^{11}_{110}(k) + \tilde{h}^{11}_{111}(k). \tag{39}$$

These equations generalize well-known results for polar nonpolarizable fluids.[16,18–20] (The often-used Δ and D subscript notation originates in Wertheim's solution of the MSA for dipolar hard spheres.[21]) Additionally, the orthogonal polynomial expansions also afford a direct route to the free energy and chemical potential.[22]

III. SAMPLE CALCULATIONS

We have calculated the thermodynamic, dielectric, and structural properties of a system of polar polarizable Lennard-Jones atoms for several states for which molecular dynamics (MD) data are available.[23–25] These calculations follow the integral equation procedures described above, using three specific closures: optimized reference-hypernetted chain (RHNC),[26–28] hypernetted chain (HNC),[12] and single superchain (SSC),[29] also known as linearized HNC (LHNC). In the numerical work, integrals over r are evaluated using the trapezoidal rule on a grid of $N_r = 1024$ points with an interval $\Delta r/\sigma = 0.02$. Similarly, integrals over k are evaluated using the trapezoidal rule and N_r points, with an interval $\Delta k = \pi/N_r\Delta r$. The fivefold Gaussian quadratures for the expansion coefficients, Eq. (21), are carried out with $\nu = 10$ points each (see Appendix C). To accelerate convergence, we use the Newton–Raphson iteration scheme of Labík, Malijevský, and Voňka[30,31] to solve the OZ equation for the coefficients $\tilde{\gamma}^{00}_{000}(k)$, $\tilde{\gamma}^{11}_{110}(k)$, and $\tilde{\gamma}^{11}_{111}(k)$, as well as the Ng predictor[32] for all $\gamma^{n_1n_2}_{l_1l_2m}(r)$.

In this work, we use the simplest version of the optimized RHNC closure, a spherically symmetric hard sphere bridge function: $B(\mathbf{r},\mathbf{m}_1,\mathbf{m}_2) \approx B_{\mathrm{HS}}(r)$.

The thermodynamic properties computed are the internal energy $U = U_0 + U_{dd}$, where

$$U_0/N = \tfrac{1}{2}\rho\int d\mathbf{r} g^{00}_{000}(r)u_0(r), \tag{40}$$

$$U_{dd}/N = \tfrac{1}{2}\rho\int d\mathbf{r}\sum_{m=-1,0,1} g^{11}_{11m}(r)u^{11}_{11\bar{m}}(r), \tag{41}$$

and the pressure $p = p_0 + p_{dd}$, where

$$\beta p_0/\rho = 1 - \tfrac{1}{6}\rho\int d\mathbf{r} g^{00}_{000}(r) r\frac{d\beta u_0(r)}{dr}, \tag{42}$$

and $\beta p_{dd}/\rho = \beta U_{dd}/N$. From among the electrostatic properties due to u_{dd}, we calculate ξ_2 and ξ_4 from Eq. (26), the rescaled parameters μ and α from Eqs. (29)–(30), the effective dipole moment,

$$m_e \equiv \langle m^2\rangle^{1/2} = (\mu^2 + 3\alpha k_BT)^{1/2}, \tag{43}$$

and finally the dielectric constant ϵ from the $\tilde{h}^{11}_{11m}(0)$. It will be noted that $\xi_2 = \beta U_{dd}/N$.

Table I lists the results for MD cases reported by Pollock, Alder, and Patey[23] for a state near the triple point density, $\rho\sigma^3 = 0.8$ and $k_BT/\varepsilon = 1.35$. The three closures give generally similar results.[33] Where the disparities are greatest, the RHNC value gives the closest agreement with simula-

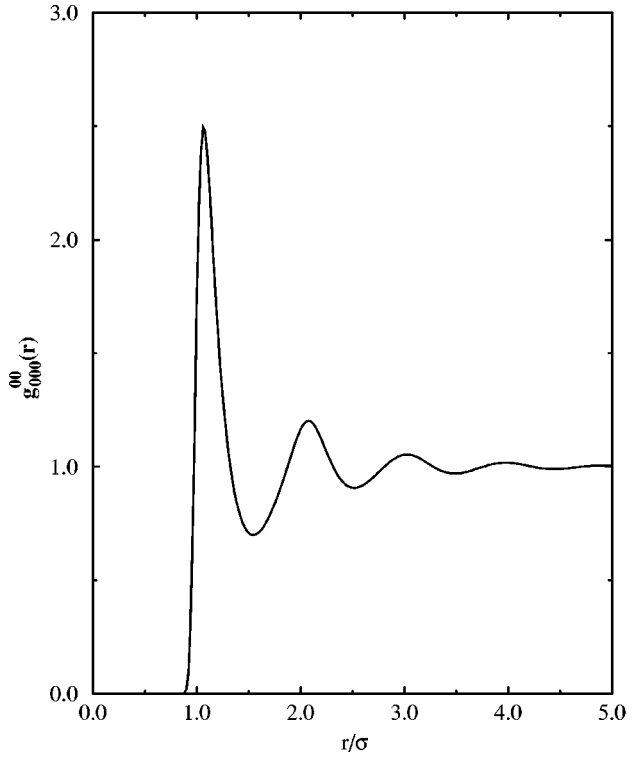

FIG. 3. Radial distribution function $g^{00}_{000}(r)$ of a polar polarizable Lennard-Jones liquid at density $\rho\sigma^3 = 0.80$ and temperature $k_BT/\varepsilon = 1.35$. The computed results using the RHNC equation with permanent dipole moment $\mu_0/(\varepsilon\sigma^3)^{1/2} = 0.50$ and polarizabilities $\alpha_0/\sigma^3 = 0$ and 0.075. The two curves are indistinguishable on this scale.

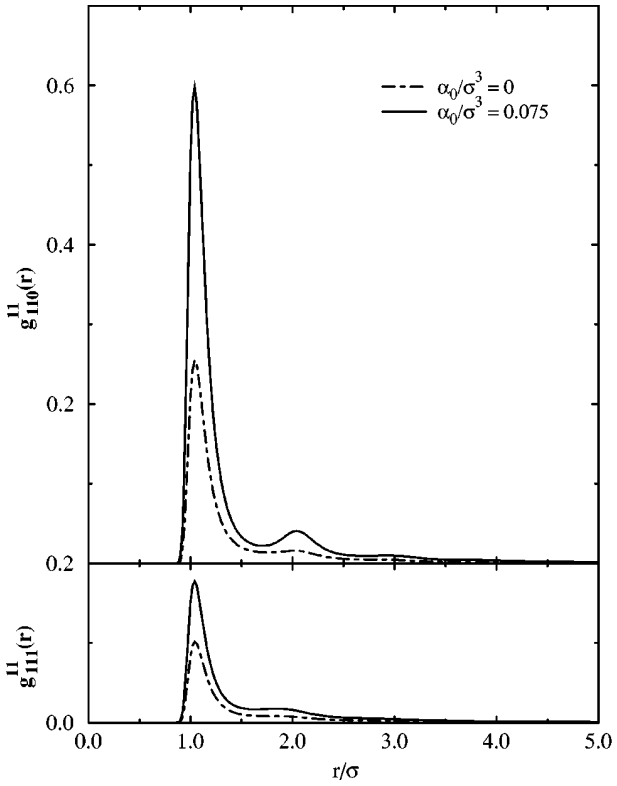

FIG. 4. Coefficients $g^{11}_{110}(r)$ and $g^{11}_{111}(r)$ of the pair distribution function $g(\mathbf{r},\mathbf{m}_1,\mathbf{m}_2)$ for a polar polarizable Lennard-Jones liquid at density $\rho\sigma^3 = 0.80$ and temperature $k_BT/\varepsilon = 1.35$. The computed results using the RHNC equation with permanent dipole moment $\mu_0/(\varepsilon\sigma^3)^{1/2} = 0.50$ and polarizabilities $\alpha_0/\sigma^3 = 0$ and 0.075.

tion. We note that the ''effective moment'' computed in MD simulations does not include thermal fluctuations[34] and so corresponds here to μ rather than m_e.

For the smaller dipole moment in Table I, the electrostatic effect of increasing the polarizability from 0 to $0.075\sigma^3$ is to double the dielectric constant ϵ. In Figures 3 and 4 we show the corresponding structural effects. One sees that the geometrical packing of the atoms, reflected in the radial distribution functions of Figure 3, is hardly affected by the increase in polarizability; the two curves are not distinguishable on this scale. However, the principal electrostatic coefficients of $g(\mathbf{r}_{12},\mathbf{m}_1,\mathbf{m}_2)$ (which determine ϵ), shown in Figure 4, are greatly increased in amplitude. This behavior agrees qualitatively with simulation findings[23,34] and is representative in general of the computed results.

For the state with $\mu_0/(\varepsilon\sigma^3)^{1/2}=1.50$ and $\alpha_0/\sigma^3=0.025$ in Table I, the maximum index n,l,m had to be reduced to 2 to achieve convergence of the RHNC and HNC equations (and so there is no ξ_4 value). Of course, the SSC equation uses only the three coefficients with $n,l,m\leqslant 1$ in any case. No converged solution of the RHNC or HNC equation was found for the next state reported by Pollock *et al.*, $\alpha_0/\sigma^3=0.050$ for the same μ_0. Although the last state for which a solution was obtained lies in the neighborhood of the two-phase region,[35] the pressure remains positive and there is no sign of divergence in the isothermal compressibility. Inspection of the dependence of the dielectric constant on α_0, shown in Figure 5, reveals that the end point of the curve approaches a vertical slope, which could be an indication of the presence of a real double solution. The existence of double solutions is a known feature of this type of problem[36] that indicates the onset of complex solutions. In the framework of linear approximations like the SSC or the

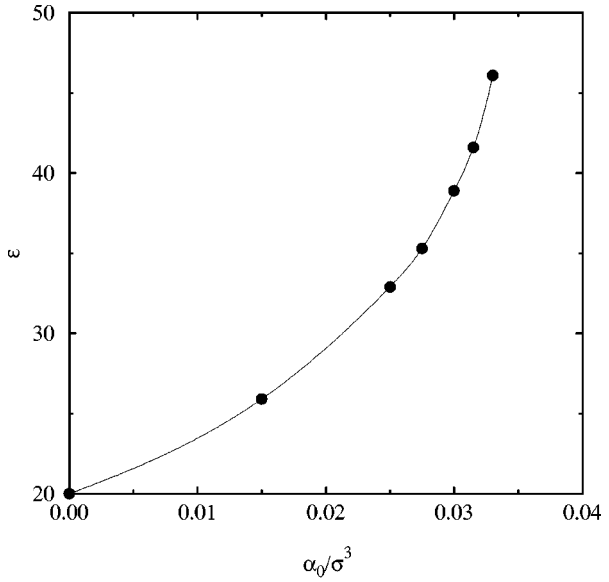

FIG. 5. Variation of the dielectric constant ϵ with polarizability α_0 for a polar polarizable Lennard-Jones liquid at density $\rho\sigma^3 = 0.80$ and temperature $k_BT/\varepsilon = 1.35$. The computed results using the HNC equation with permanent dipole moment $\mu_0/(\varepsilon\sigma^3)^{1/2} = 1.50$.

TABLE II. Computed thermodynamic and electrostatic properties of a polar polarizable Lennard-Jones fluid for $\rho\sigma^3 = 0.80$ and $\mu_0/(\varepsilon\sigma^3)^{1/2} = 1.50$. Molecular dynamics data are from Weis and Levesque (Ref. 24). Estimated errors in the simulation ϵ are $\pm 10\%$.

k_BT/ε	α_0/σ^3		$U_0/N\varepsilon$	$U_{dd}/N\varepsilon$	$\beta p/\rho$	ξ_2	ξ_4	$\mu/(\varepsilon\sigma^3)^{1/2}$	α/σ^3	$m_e/(\varepsilon\sigma^3)^{1/2}$	ϵ
1.71	0	MD	−4.72	−2.72	2.11			1.50			12.9
		RHNC	−4.816	−2.623	2.041	0	0	1.50	0	1.50	13.0
		HNC	−4.481	−2.714	3.249	0	0	1.50	0	1.50	12.8
		SSC	−4.639	−2.783	2.636	0	0	1.50	0	1.50	14.9
1.72	0.025	MD	−4.62	−3.56	1.92			1.61			18
		RHNC	−4.726	−3.490	1.841	−2.0287	0.0657	1.603	0.0267	1.646	18.1
		HNC	−4.388	−3.647	3.005	−2.1203	0.0818	1.608	0.0268	1.650	18.4
		SSC	−4.631	−3.661	2.140	−2.1282	0	1.608	0.0268	1.650	21.8
1.74	0.050	MD	−4.48	−4.85	1.62			1.76			26
		RHNC	−4.572	−4.873	1.546	−2.8007		1.753	0.0584	1.838	28.8
		HNC	−4.215	−5.231	2.633	−3.0066		1.769	0.0590	1.854	36.7
		SSC	−4.614	−4.972	1.424	−2.8575	0	1.757	0.0586	1.842	36.0

MSA, these complex solutions can be understood as the origin of optical absorption[36] when a frequency dependent polarizability model is used. In the context of our nonlinear approach this is however less clear.

A solution for the state with $\mu_0/(\varepsilon\sigma^3)^{1/2} = 1.50$ and $\alpha_0/\sigma^3 = 0.050$ can be found if one raises the temperature. This is shown in Table II[33] along with the MD data of Weis and Levesque.[24] The parameter ξ_4 is not listed for this polarizability since once again the maximum index in the RHNC and HNC solutions had to be reduced to 2 to achieve convergence.

From the extensive data of Kriebel and Winkelmann,[25] we have selected high temperature states, $k_BT/\varepsilon = 3$, with permanent dipole moment $\mu_0/(\varepsilon\sigma^3)^{1/2} = 1$. These data (which do not include the dielectric constant) are listed in Table III for three values of the polarizability and a range of densities, along with the corresponding computed results from just the RHNC closure. The overall agreement is seen to be reasonably good.

Improvement of the RHNC results can be made by using a generalized reference system yielding a dipole-dependent bridge function $B(\mathbf{r},\mathbf{m}_1,\mathbf{m}_2)$, rather than the simple spherically-symmetric $B_{\mathrm{HS}}(r)$ used here.

The exact expansion for $F(m)$ given by Eq. (25), with coefficients ξ_{2j}, is found by calculation to be very rapidly convergent. In fact, with ξ_4 some two orders of magnitude smaller than ξ_2 in all computable cases, $F(m)$ retains essentially the same form as $F_0(m)$, with rescaled parameters α and μ.

TABLE III. Computed thermodynamic and electrostatic properties of a polar polarizable Lennard-Jones fluid for $k_BT/\varepsilon=3$ and $\mu_0/(\varepsilon\sigma^3)^{1/2}=1$. Molecular dynamics data are from Kriebel and Winkelmann (Ref. 25). The simulation uncertainties in the last digits are given in parentheses.

$\rho\sigma^3$	α_0/σ^3		$U/N\varepsilon$	$p\sigma^3/\varepsilon$	ξ_2	ξ_4	$\mu/(\varepsilon\sigma^3)^{1/2}$	α/σ^3	$m_e/(\varepsilon\sigma^3)^{1/2}$	ϵ
0.2	0.02	MD	−1.319(5)	0.600(2)			1.006			
		RHNC	−1.358	0.597	−0.0605	0.0009	1.006	0.0201	1.092	1.37
	0.04	MD	−1.355(5)	0.588(2)			1.015			
		RHNC	−1.424	0.590	−0.0828	0.0020	1.014	0.0406	1.181	1.44
	0.06	MD	−1.377(5)	0.591(2)			1.027			
		RHNC	−1.505	0.583	−0.1100	0.0041	1.025	0.0615	1.267	1.52
0.4	0.02	MD	−2.604(5)	1.445(8)			1.013			
		RHNC	−2.664	1.450	−0.1204	0.0013	1.012	0.0202	1.098	1.83
	0.04	MD	−2.651(4)	1.438(5)			1.031			
		RHNC	−2.795	1.421	−0.1661	0.0032	1.029	0.0411	1.195	2.01
	0.06	MD	−2.706(5)	1.405(6)			1.055			
		RHNC	−2.959	1.387	−0.2236	0.0066	1.051	0.0630	1.293	2.23
0.6	0.02	MD	−3.804(6)	3.419(14)			1.019			
		RHNC	−3.900	3.390	−0.1853	0.0013	1.019	0.0204	1.105	2.38
	0.04	MD	−3.887(5)	3.352(11)			1.048			
		RHNC	−4.104	3.315	−0.2577	0.0035	1.044	0.0418	1.211	2.74
	0.06	MD	−3.966(5)	3.272(12)			1.086			
		RHNC	−4.366	3.219	−0.3510	0.0077	1.078	0.0647	1.321	3.18
0.8	0.02	MD	−4.702(6)	8.494(20)			1.027			
		RHNC	−4.840	8.421	−0.2591	0.0011	1.026	0.0205	1.112	3.04
	0.04	MD	−4.806(4)	8.364(18)			1.067			
		RHNC	−5.135	8.260	−0.3640	0.0033	1.062	0.0425	1.288	3.68
	0.06	MD	−4.936(6)	8.215(25)			1.122			
		RHNC	−5.526	8.046	−0.5031	0.0077	1.110	0.0666	1.353	4.51

IV. CONCLUSION

This work is motivated by the sense that internal degrees of freedom in classical liquids should be manageable in much the same way as are orientational degrees of freedom: through expansions in special orthogonal functions tailored to the specific cases. When the internal variable, such as the fluctuating dipole moment **m** treated in this paper, has a distribution $F(m)$, this means polynomials orthogonal with weight function $F(m)$. Given these polynomials, one can construct an algorithm for the iterative solution of the mutually dependent microscopic liquid structure, as described by the pair distribution function $g(\mathbf{r},\mathbf{m},\mathbf{m}')$, and the ''internal structure,'' as described by the distribution function $F(m)$, with no further approximations beyond that of some closure relation familiar from simple classical liquids.

This program was carried out recently[3] for liquids of nonpolar polarizable molecules. Compared to earlier integral equation studies of fluids of polar nonpolarizable molecules,[15] the cost of polarizabilty is an additional two degrees of freedom in the pair functions and so two additional indices in the expansion coefficients, a manageable increase in numerical complexity. In this paper, we have extended the technique to polar polarizable molecules and find *no further increase in complexity*. The orthogonal polynomial method makes polar polarizable fluids as easy to study as nonpolar polarizable systems. In programming terms, one merely replaces the subroutine that calculates the orthogonal polynomials.

It seems likely that the same approach will be usable with other internal degrees of freedom, such as fluctuating bond lengths and angles in polyatomic molecules. In particular, the simplest such model, a flexible diatomic molecule, should be accessible with yet again the identical formalism as in this paper and Ref. 3, using yet another set of polynomials Q_{nl}.

ACKNOWLEDGMENTS

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APPENDIX A: MOMENTS $\langle m^{2j}\rangle$ OF $F(m)$

The distribution function

$$F(m)=\frac{\exp[-\beta(m^2+\mu^2)/2\alpha]}{(2\pi\alpha/\beta)^{3/2}}\,\frac{\sinh(\beta\mu m/\alpha)}{\beta\mu m/\alpha} \tag{A1}$$

is a symmetric function of **m** and so has only even moments. It is convenient to calculate these in dimensionless form. Put $x^2=\beta m^2/2\alpha$ and $x_0^2=\beta\mu^2/2\alpha$; we seek

$$\langle x^{2j}\rangle=\langle(\beta m^2/2\alpha)^j\rangle. \tag{A2}$$

These can be quickly found by evaluating the moment generating function,[37]

$$\begin{aligned}\langle e^{ikx^2}\rangle&=\int d\mathbf{m}F(m)\exp(ik\beta m^2/2\alpha)\\&=\frac{2e^{-x_0^2}}{\sqrt{\pi}x_0}\int_0^\infty dx x e^{-(1-ik)x^2}\sinh(2x_0x)\\&=\frac{\exp[ikx_0^2/(1-ik)]}{(1-ik)^{3/2}}.\end{aligned} \tag{A3}$$

The final equality in (A3) is recognized as the generating function of the associated Laguerre polynomials,[9] so we have

$$\langle e^{ikx^2}\rangle=\sum_{j=0}^{\infty}L_j^{1/2}(-x_0^2)(ik)^j=\sum_{j=0}^{\infty}\frac{\langle x^{2j}\rangle}{j!}(ik)^j, \tag{A4}$$

whence

$$\langle x^{2j}\rangle=j!L_j^{1/2}(-\beta\mu^2/2\alpha). \tag{A5}$$

APPENDIX B: POLYNOMIALS $Q_{nl}(m)$ OF $F(m)$

In a straightforward application of the Gram–Schmidt method,[9] we begin with $Q_{00}(m)=1$ and construct the next polynomial with $l=0$ as $Q_{20}(m)=a(b-x^2)$, where $x^2=\beta m^2/2\alpha$. Then orthogonality requires

$$\langle Q_{00}(m)Q_{20}(m)\rangle=a(b-\langle x^2\rangle)=0 \tag{B1}$$

or $b=\langle x^2\rangle$, while normalization leads to

$$\langle Q_{20}^2(m)\rangle=a^2[\langle x^2\rangle^2-2\langle x^2\rangle^2+\langle x^4\rangle]=1 \tag{B2}$$

or $a=1/[\langle x^4\rangle-\langle x^2\rangle^2]^{1/2}$. Thus we find

$$Q_{20}(m)=\frac{\langle x^2\rangle-x^2}{[\langle x^4\rangle-\langle x^2\rangle^2]^{1/2}}=\frac{-1}{(D_{00}D_{20})^{1/2}}\begin{vmatrix}1 & \langle x^2\rangle\\ 1 & x^2\end{vmatrix}. \tag{B3}$$

In the second equality of (B3), we have used two determinants D_{nl}, defined in general for $n=l,l+2,l+4,\ldots,$ by

$$D_{nl}=\begin{vmatrix}\langle x^{2l}\rangle & \langle x^{2l+2}\rangle & \cdots & \langle x^{l+n}\rangle\\ \langle x^{2l+2}\rangle & \langle x^{2l+4}\rangle & \cdots & \langle x^{l+n+2}\rangle\\ \cdot & \cdot & \cdots & \cdot\\ \cdot & \cdot & \cdots & \cdot\\ \cdot & \cdot & \cdots & \cdot\\ \langle x^{l+n}\rangle & \langle x^{l+n+2}\rangle & \cdots & \langle x^{2n}\rangle\end{vmatrix}, \tag{B4}$$

which we supplement with $D_{l-2,l}\equiv 1$ for later convenience. For n even, the general expression for $Q_{n0}(m)$ is given by Akhiezer[10] as

$$Q_{n0}(m)=\frac{(-1)^{n/2}}{(D_{n-2,0}D_{n0})^{1/2}} \times \begin{vmatrix} 1 & \langle x^2\rangle & \cdots & \langle x^n\rangle \\ \langle x^2\rangle & \langle x^4\rangle & \cdots & \langle x^{n+2}\rangle \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \langle x^{n-2}\rangle & \langle x^n\rangle & \cdots & \langle x^{2n-2}\rangle \\ 1 & x^2 & \cdots & x^n \end{vmatrix}. \quad \text{(B5)}$$

A similar procedure is followed for higher l values. Thus, the sequence for $l=1$ begins with $Q_{11}(m)=x/\langle x^2\rangle^{1/2}$; $Q_{31}(m)=ax(b-x^2)$ is then constructed to be orthogonal to $Q_{11}(m)$ and normalized to unity. For brevity, we simply list here the nine polynomials actually used in the calculation:

$$Q_{00}(m)=\frac{1}{(D_{-20}D_{00})^{1/2}}=1, \quad \text{(B6)}$$

$$Q_{20}(m)=\frac{-1}{(D_{00}D_{20})^{1/2}}\begin{vmatrix} 1 & \langle x^2\rangle \\ 1 & x^2 \end{vmatrix}, \quad \text{(B7)}$$

$$Q_{40}(m)=\frac{1}{(D_{20}D_{40})^{1/2}}\begin{vmatrix} 1 & \langle x^2\rangle & \langle x^4\rangle \\ \langle x^2\rangle & \langle x^4\rangle & \langle x^6\rangle \\ 1 & x^2 & x^4 \end{vmatrix}, \quad \text{(B8)}$$

$$Q_{11}(m)=\frac{x}{(D_{-11}D_{11})^{1/2}}, \quad \text{(B9)}$$

$$Q_{31}(m)=\frac{-x}{(D_{11}D_{31})^{1/2}}\begin{vmatrix} \langle x^2\rangle & \langle x^4\rangle \\ 1 & x^2 \end{vmatrix}, \quad \text{(B10)}$$

$$Q_{22}(m)=\frac{x^2}{(D_{02}D_{22})^{1/2}}, \quad \text{(B11)}$$

$$Q_{42}(m)=\frac{-x^2}{(D_{22}D_{42})^{1/2}}\begin{vmatrix} \langle x^4\rangle & \langle x^6\rangle \\ 1 & x^2 \end{vmatrix}, \quad \text{(B12)}$$

$$Q_{33}(m)=\frac{x^3}{(D_{13}D_{33})^{1/2}}, \quad \text{(B13)}$$

$$Q_{44}(m)=\frac{x^4}{(D_{24}D_{44})^{1/2}}. \quad \text{(B14)}$$

This set of polynomials gives rise to 49 distinct coefficients $X^{n_1n_2}_{l_1l_2m}$; truncating the expansions instead at a maximum n,l,m of 3, 2, 1, or 0 leads, respectively, to 22, 10, 3, or 1 coefficients. The set of 22 coefficients with a maximun index of 3 is generally adequate.

The moments $\langle x^{2j}\rangle$ are given in Appendix A. For vanishing μ_0 and so a Gaussian weight function, they become

$$\langle x^{2j}\rangle=\frac{(2j+1)!}{2^{2j}j!} \quad (\mu_0=0), \quad \text{(B15)}$$

and the polynomials Q_{nl} reduce to a classical set.[3,8]

APPENDIX C: GAUSSIAN QUADRATURE USING THE ZEROES OF $Q_{2\nu,0}(m)$

Integrals over the dipole moment m are evaluated using Gaussian quadrature based on the ν zeroes m_k of $Q_{2\nu,0}(m)$,[10]

$$4\pi\int_0^\infty dm m^2F(m)g(m)\approx\sum_{k=1}^{\nu}w_kg(m_k), \quad \text{(C1)}$$

with the weights

$$w_k=\frac{1}{\sum_{j=0}^{\nu-1}Q^2_{2j,0}(m_k)}. \quad \text{(C2)}$$

Equation (C1) is exact if $g(m)$ is a polynomial of m^2 of degree $2\nu-1$ or less. This preserves the orthonormality of the polynomials used in the numerical calculation,

$$\delta_{nn'}=4\pi\int_0^\infty dm m^2F(m)Q_{nl}(m)Q_{n'l}(m) =\sum_{k=1}^{\nu}w_kQ_{nl}(m_k)Q_{n'l}(m_k), \quad \text{(C3)}$$

for $n,n'<2\nu$.

In principle, the initiation steps for use of this rule are as follows

1. Calculate $\langle x^{2j}\rangle$ and $D_{2j,0}$ for $j=0,1,2,\ldots,\nu$.
2. Calculate $Q_{2\nu,0}(m)$ and find its roots m_k, $k=1,2,\ldots,\nu$, using, say, Newton's method.
3. Compute the weights w_k from Eq. (C2).

In practice, one finds that the moments $\langle x^{2j}\rangle$ grow exponentially fast because of the $j!$ in Eq. (A5); to avoid the loss of accuracy this causes in finite precision arithmetic, the *reduced* quantities $\langle x^{2j}\rangle/j!$ and $D_{2j,0}/[0!2!\cdots(2j)!]$ are instead computed in step 1 and the appropriate changes are made in Eq. (B5) to get the $Q_{2j,0}(m)$ from these reduced quantities for use in steps 2 and 3. The numerical orthonormality of the $Q_{nl}(m_k)$, Eq. (C3), to double-precision accuracy (8 bytes) is ensured by carrying out these preliminary steps in quadruple precision (16 bytes).

The Gaussian quadratures for the Euler angle integrations have been described earlier.[14]

[1] An example of the flexibility of simulation programming is the DL_POLY program, a package of molecular dynamics simulation routines written by W. Smith and T. R. Forester. Copyright: The Engineering and Physical Sciences Research Council, acting through its Daresbury and Rutherford Appleton Laboratory at Daresbury Laboratory, 1994.
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