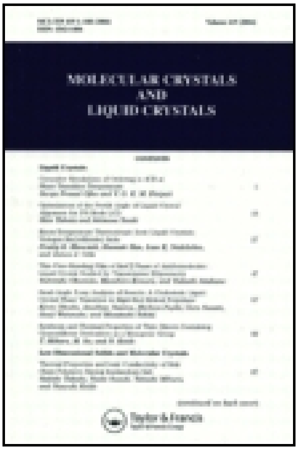

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Consistency of Mean Field Theories of Nematic Liquid Crystals

Martha A. Cotter [a] [b] [c]
[a] Bell Laboratories, Murray Hill, New Jersey, 07974
[b] Alfred P. Sloan Foundation Research Fellow
[c] School of Chemistry, Rutgers University, New Brunswick, New Jersey, 08903

Version of record first published: 28 Mar 2007.

To cite this article: Martha A. Cotter (1977): Consistency of Mean Field Theories of Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals, 39:1-2, 173-181

To link to this article: http://dx.doi.org/10.1080/15421407708083918

Mol. Cryst. Liq. Cryst., 1977, Vol. 39, pp. 173–181

Printed in Holland

Consistency of Mean Field Theories of Nematic Liquid Crystals

MARTHA A. COTTER†‡
Bell Laboratories§, Murray Hill, New Jersey, 07974

(*Received October 6, 1976; in final form November 15, 1976*)

The Maier–Saupe theory of nematic liquid crystals, which uses a one-body mean field potential of the form $\bar{\psi}_2 \eta P_2(\cos\theta)$, where θ is the angle between the molecular long axis and the nematic director and η is the average value of the Legendre polynomial $P_2(\cos\theta)$, is shown to exhibit statistical-thermodynamic self-consistency if and only if $\bar{\psi}_2$ is independent of the temperature and directly proportional to the first power of the density. The significance of this result with respect to a molecular theory of the nematic state is discussed.

1 INTRODUCTION

Nematic mesophases are the simplest of all liquid crystalline phases: they differ from ordinary isotropic liquids only in their possession of long-range orientational order, with the molecular long axes tending to align parallel to a space-fixed axis called the director. On a phenomenological level, their physical properties are well-understood. On the molecular level, however, our understanding of the mechanism by which interactions between the rodlike component molecules produce nematic order is still incomplete. In particular, the relative importance of very short-ranged anisotropic intermolecular repulsions versus relatively longer-ranged anisotropic attractive forces is still the subject of some controversy.[1]

The most widely quoted molecular theory of nematics is the mean field theory of Maier and Saupe.[2] Assuming that nematic order is due solely to the anisotropic part of the intermolecular dispersion forces (London forces),

---

† Alfred P. Sloan Foundation Research Fellow.

‡ Permanent address: School of Chemistry, Rutgers University, New Brunswick, New Jersey 08903.

§ Resident Visitor 1975–76.

MS adopted a pseudo-potential of the form

$$\bar{\psi}_a = \bar{\psi}_2 \eta P_2(\cos\theta)$$

(my notation) to describe the orientational potential energy of a molecule in the "mean field" of its neighbors, where θ is the angle between the molecular long axis and the nematic director; the orientational order parameter η is the average value of the Legendre polynomial $P_2(\cos\theta)$; and $\bar{\psi}_2$ was set equal to $-A\rho^2$ $(A > 0)$. The theory predicts a first-order transition from the isotropic liquid to a stable nematic phase at a temperature T_c. When the constant A is chosen to reproduce experimentally observed T_c's, order parameter versus temperature curves in very good qualitative agreement with experiment are obtained. The approach has been extended[3] by adding a term $\bar{\psi}_4 \delta P_4(\cos\theta)$ (δ is the average value of $P_4(\cos\theta)$) to the original pseudo-potential and it has been demonstrated[4,5] that with certain choices for $\bar{\psi}_2(\rho)$ and $\bar{\psi}_4(\rho)$, it is possible to predict the temperature and density dependence of the order parameter η quantitatively.

In the present paper, it will be shown that the sort of pseudo-potential needed to obtain such quantitative agreement with experiment[6] (i.e., $\bar{\psi}_2 \propto \rho^4$) leads to statistical thermodynamic inconsistency, as does any choice for the coefficient $\bar{\psi}_2(\rho)$ other than $\bar{\psi}_2 \propto \rho$. The consistency requirements are derived in Section II. Their implications with respect to a molecular understanding of the nematic state are discussed in Section III.

II CONSISTENCY REQUIREMENTS

A nematic liquid crystal or its isotropic liquid may be viewed as a fluid of classical, effectively cylindrically symmetric molecules. For N such entities contained in a volume V, the configurational partition function Q_N, n-particle distribution function $\rho^{(n)}$, and n-particle correlation function $g^{(n)}$ can be written

$$Q_N = \frac{\int\cdots\int \exp(-\beta U_N)\mathrm{d}\gamma_1\cdots\mathrm{d}\gamma_N}{N!(4\pi)^N} \equiv \frac{Z_N}{N!(4\pi)^N}. \tag{1}$$

$$\rho^{(n)}(\mathbf{r}_1,\Omega_1,\ldots,\mathbf{r}_n,\Omega_n) = \frac{N!\int\cdots\int \exp(-\beta U_N)\mathrm{d}\gamma_{n+1}\cdots\mathrm{d}\gamma_N}{(N-n)!Z_N}, \tag{2}$$

$$g^{(n)} = \frac{\rho^{(n)}}{\prod_{i=1}^{n}\rho^{(1)}(\mathbf{r}_i,\Omega_i)}, \tag{3}$$

where U_N is the N-particle configurational potential energy, $\mathbf{r}_i$ and Ω_i denote, respectively, the position and orientation of molecule i, $\beta = 1/kT$,

$\rho = N/V$, and $d\gamma_i = d\mathbf{r}_i \sin\theta_i \, d\theta_i \, d\varphi_i$.[7] Since the system is a fluid,

$$\rho^{(1)}(\mathbf{r}_1, \Omega_1) = \rho f(\Omega_1), \tag{4}$$

$$\rho^{(2)}(\mathbf{r}_{12}, \Omega_1, \Omega_2) = \rho^2 f(\Omega_1) f(\Omega_2) g^{(2)}(\mathbf{r}_{12}, \Omega_1, \Omega_2). \tag{5}$$

The orientational distribution function $f(\Omega)$ can, therefore, be defined formally by

$$f(\Omega_1) = \frac{V}{Z_N} \int \cdots \int \exp(-\beta U_N) d\gamma_2 \cdots d\gamma_N. \tag{6}$$

In mean field theories of the nematic state, the orientation-dependent interactions of a molecule with its neighbors are replaced by its interaction with a mean field, and all the thermodynamic properties of the system are obtained from the effective one-body potential or pseudo-potential $\bar{\psi}_a(\Omega)$ defined by

$$\bar{\psi}_a(\Omega_i) = \sum_{j \neq i} \overline{v_a(\mathbf{r}_{ij}, \Omega_i, \Omega_j)},$$

where $\bar{v}_a$ is the average value of the orientation-dependent part of the intermolecular pair potential $v(\mathbf{r}_{ij}, \Omega_i, \Omega_j) = v_0(r_{ij}) + v_a(\mathbf{r}_{ij}, \Omega_i, \Omega_j)$. In particular, the orientational distribution function, mean internal energy, and entropy, respectively, are given by

$$f(\Omega) = \frac{\exp(-\beta\bar{\psi}_a)}{\int \exp(-\beta\bar{\psi}_a) d\Omega} \tag{7}$$

$$\frac{U_a}{N} = \frac{U(\eta)}{N} - \frac{U(0)}{N} = \frac{1}{2} \int \bar{\psi}_a(\Omega) f(\Omega) d\Omega \tag{8}$$

$$\frac{S_a}{Nk} = \frac{S(\eta)}{Nk} - \frac{S(0)}{Nk} = -\int f(\Omega) \ln[4\pi f(\Omega)] d\Omega \tag{9}$$

As noted previously, the simplest version of the theory[2,8] uses a pseudo-potential

$$\bar{\psi}_a = \bar{\psi}_2 \eta P_2(\cos\theta), \tag{10}$$

where θ is the angle between the molecular long axis and the so-called director or "preferred" axis,[9] η is the orientational order parameter defined by $\eta = \int P_2(\cos\theta) f(\Omega) d\Omega$, and $\bar{\psi}_2$ is negative since the nematic order is assumed to arise from anisotropic dispersion forces. It will now be shown that a pseudo-potential of this form leads to statistical-thermodynamic consistency if and *only* if $\bar{\psi}_2$ is temperature-independent and directly proportional to the density.

First, substituting $\bar{\psi}_a$ from (10) into (7), (8), and (9), one obtains

$$f(\Omega) = \frac{\exp\{-\beta\bar{\psi}_2\eta P_2(\cos\theta)\}}{2\pi\zeta} \tag{11}$$

$$\frac{U_a}{N} = \frac{1}{2}\bar{\psi}_2\eta^2, \tag{12}$$

$$\frac{S_a}{Nk} = \beta\bar{\psi}_2\eta^2 + \ln\left(\frac{\zeta}{2}\right) \tag{13}$$

where $\zeta = \int_0^\pi \exp[-\beta\bar{\psi}_2\eta P_2(\cos\theta)]\sin\theta\,d\theta$. The order-dependent Helmholtz free energy A_a is then given by

$$\frac{A_a}{N} = \frac{U_a}{N} - \frac{TS_a}{N} = -\frac{1}{2}\bar{\psi}_2\eta^2 - kT\ln\left(\frac{\zeta}{2}\right). \tag{14}$$

From these expressions, it is easily seen that $\bar{\psi}_2$ must be independent of temperature at constant density, since otherwise the expression for S_a obtained by differentiating (14) with respect to T at constant ρ will not be consistent with (13).

The required density dependence of $\bar{\psi}_2$ can be derived using a method devised by Widom,[10] who first noted that

$$\begin{aligned} Z_N &= \int\cdots\int \exp(-\beta\psi)\exp(-\beta U_{N-1})d\gamma_1\cdots d\gamma_N \\ &= Z_{N-1}\int\langle\exp(-\beta\psi)\rangle d\gamma_1 \\ &= 4\pi V Z_{N-1}\langle\!\langle\exp(-\beta\psi)\rangle\!\rangle \end{aligned} \tag{15}$$

where $\psi(\gamma_1, \ldots, \gamma_N)$ is the total interaction energy of a molecule at $\mathbf{r}_1$ with orientation Ω_1 with all of its neighbors, $\langle\ \ \rangle$ denotes the ensemble average over the $N-1$ particle system $(2, 3, \ldots, N)$, and $\langle\!\langle\ \ \rangle\!\rangle$ denotes averaging over γ_1 as well, assigning equal weights to equal volume elements in the 1-particle phase space. Moreover, it is easily shown that

$$z = \frac{4\pi N Z_{N-1}}{Z_N} = \frac{\rho}{\langle\!\langle\exp(-\beta\psi)\rangle\!\rangle}, \tag{16}$$

$$\frac{U}{N} = \frac{1}{2}\frac{\langle\!\langle\psi\exp(-\beta\psi)\rangle\!\rangle}{\langle\!\langle\exp(-\beta\psi)\rangle\!\rangle} \tag{17}$$

$$= \frac{1}{2}\frac{z}{\rho}\langle\!\langle\psi\exp(-\beta\psi)\rangle\!\rangle, \tag{18}$$

$$f(\Omega_1) = \frac{\langle\exp(-\beta\psi)\rangle}{4\pi\langle\!\langle\exp(-\beta\psi)\rangle\!\rangle}, \tag{19}$$

where z is the thermodynamic activity defined so that $z \to \rho$ as $\rho \to 0$. Comparing Eqs. (7) and (19), it is clear that the mean field approximation consists in replacing at least the orientation-dependent part ψ_a of the one-body energy ψ by its mean value in the ensemble average $\langle \exp(-\beta\psi)\rangle$; i.e., in assuming that

$$\langle \exp[-\beta(\psi_0 + \psi_a)]\rangle \approx \exp(-\beta\psi_a)\langle \exp(-\beta\psi_0)\rangle.$$

where $\psi = \psi_0 + \psi_a$. In this approximation, therefore,

$$\begin{aligned} z &= \frac{\rho}{\iint (\mathrm{d}\mathbf{r}/V)(\mathrm{d}\Omega/4\pi)\exp(-\beta\bar{\psi}_a)\langle \exp(-\beta\bar{\psi}_0)\rangle} \\ &= \frac{\rho}{\{\langle\!\langle \exp(-\beta\psi_0)\rangle\!\rangle \int (\mathrm{d}\Omega/4\pi)\exp(-\beta\bar{\psi}_a)\}} \end{aligned} \tag{20}$$

and with $\bar{\psi}_a$ given by (10),

$$\ln z_a = \ln z(\eta) - \ln z(0) = -\ln\left(\frac{\zeta}{2}\right) \tag{21}$$

To achieve self-consistency, (12) and (21) must satisfy the thermodynamic identity[10]

$$\left(\frac{\partial \ln z_a}{\partial \beta}\right)_\rho = \frac{U_a}{N} + \left(\frac{\partial (U_a/N)}{\partial \rho}\right)_\beta. \tag{22}$$

Performing the required differentiations and substitutions, this becomes

$$0 = \frac{1}{2}\eta^2\left[\bar{\psi}_2(\rho) - \rho\frac{\partial\bar{\psi}_2}{\partial\rho}\right] + \eta\bar{\psi}_2(\rho)\left[\beta\left(\frac{\partial\eta}{\partial\beta}\right)_\rho - \rho\left(\frac{\partial\eta}{\partial\rho}\right)_\beta\right] \tag{23}$$

$$= \frac{\eta^2}{2}\left[\bar{\psi}_2(\rho) - \rho\frac{\partial\bar{\psi}_2}{\partial\rho}\right]\left\{\frac{1 - \beta\bar{\psi}_2(\rho)\overline{(P_2(\cos\theta) - \eta)^2}}{1 + \beta\bar{\psi}_2(\rho)\overline{(P_2(\cos\theta) - \eta)^2}}\right\} \tag{24}$$

where $\overline{(P_2(\cos\theta) - \eta)^2} = \int [P_2(\cos\theta) - \eta]^2 f(\Omega)\mathrm{d}\Omega$. Since $\bar{\psi}_2(\rho)$ is assumed to be negative while $\overline{(P_2(\cos\theta) - \eta)^2}$ is always positive, $\bar{\psi}_2(\rho)$ must equal $\rho(\partial\bar{\psi}_2/\partial\rho)$ in order for the right-hand side of (24) to vanish. In other words, consistency will be achieved if and only if

$$\bar{\psi}_a = W_2\rho\eta P_2(\cos\theta) \tag{25}$$

where W_2 is a constant. One can come to the same conclusion, moreover, by comparing (21) with the expression for $\ln z_a$ obtained from the density derivative of (14). Finally, if one extends[3] the Maier–Saupe theory by adding a term $\bar{\psi}_4\delta P_4(\cos\theta)$ ($\delta = \overline{P_4(\cos\theta)}$) to the right-hand side of (10), then using the same arguments, it can be shown that $\bar{\psi}_4$ as well as $\bar{\psi}_2$ must have the form

$\bar{\psi}_n = W_n \rho$ where W_n is a constant. All other types of density and temperature dependence produce statistical thermodynamic inconsistency, including the ρ^2 dependence for $\bar{\psi}_2$ originally assumed by Maier and Saupe[2] and the ρ^3, ρ^4, etc. dependences used by others.[3,8]

III DISCUSSION

The implication of these results is clear: one cannot quantitatively predict the behavior of the nematic order parameter η using a self-consistent formulation of the Maier–Saupe theory or its extension by Humphries, James, and Luckhurst (HJL)[3]. A quantitative fit between theory and experiment[6] requires $\bar{\psi}_2 \propto \rho^2$, while only $\bar{\psi}_2 \propto \rho$ leads to statistical mechanical consistency.

Proponents of the Maier–Saupe approach may argue that the consistency demands imposed in Section II are unreasonably stringent; i.e., that one should choose $\bar{\psi}_2(\rho)$ on intuitive grounds (or from recourse to experiment) and then be content with the thermodynamic consistency of the expressions for S, U, P, z, etc. derived from (14), without demanding statistical mechanical consistency as well. In my opinion, however, it is not at all unreasonable to demand that a mean field theory of nematic liquids be self-consistent in the same sense as are mean field theories of isotropic liquids. In both the generalized van der Waals theory of simple liquids[11] and the Bragg–Williams treatment of the classical lattice gas,[12] the thermodynamic identity $(\partial \ln z/\partial\beta)_\rho = 1 + \rho(\partial(U/N)/\partial\rho)_\beta$ is satisfied when z and U are obtained from (16) and (17).[10] Moreover, the generalized van der Waals equation of state $P = P^* - \frac{1}{2}\alpha\rho^2$ and activity expression $\ln z = \ln z^* - \alpha\rho$ (where α is a positive constant and P^* and z^* are the pressure and activity of a system of hard spheres with density ρ) can be derived using this identity together with (16), (17), and the Gibbs–Duhem equation.[10] No one would seriously suggest that these equations be replaced by $P = P^* - c\rho^n$ and $\ln z = \ln z^* - nc\rho^{n-1}$, with n used as an adjustable parameter or chosen on the basis of the popular but unfortunately fallacious (for a fluid at least) argument that a term in the intermolecular pair potential that varies as r^{-m} should lead to a term in $\bar{\psi}$ (and U/N) proportional to $\rho^{(m/3)}$. (See the next paragraph.)

Furthermore, $\bar{\psi}_2 \propto \rho$ is not only required for self-consistency; it is also quite reasonable physically. This is most readily seen within the context of generalized van der Waals theory,[11] where the intermolecular pair potential is divided into a very short-ranged repulsive part and a longer-ranged attractive part and the latter is subjected to the mean field approximation. Assuming that the anisotropy of the short-range repulsions can be neglected and applying this approach to a model system with pair potential

$$v(r_{ij}, \Omega_i, \Omega_j) = v^*(r_{ij}) - \frac{a_0}{r_{ij}^n} - \frac{a_2}{r_{ij}^m} P_2(\cos \Omega_{ij})$$

where

$$v^*(r_{ij}) = \begin{cases} \infty & r_{ij} < \sigma \\ 0 & r_{ij} > \sigma \end{cases}$$

and a_0 and a_2 are positive constants, one obtains the Maier–Saupe equations (11) through (14) with $\bar{\psi}_a(\Omega)$ given explicitly by [13,14]

$$\begin{aligned} \bar{\psi}_a(\Omega_i) &= \rho \int d\Omega_j f(\Omega_j) \int_V d\mathbf{r}_{ij} \left\{ -\frac{a_2}{r_{ij}^m} P_2(\cos \Omega_{ij}) \right\} \exp[-\beta v^*(r_{ij})] \\ &= -\rho \int d\Omega_j f(\Omega_j) P_2(\cos \Omega_{ij}) \int_\sigma^\infty \frac{a_2}{r_{ij}^m} 4\pi r_{ij}^2 \, dr_{ij} \\ &= -\left(\frac{4\pi\sigma^{m-3}}{m-3} \right) a_2 \rho \eta P_2(\cos \theta) \end{aligned}$$

($f(\Omega)$ was assumed to be cylindrically symmetric about the director.) Clearly, $\bar{\psi}_2$ is proportional to ρ no matter what the value of m. Moreover, the density dependence of $\bar{\psi}_a$ does not change if $v^*(r_{ij})$ is replaced by a softer repulsive potential such as $v_{\text{rep}}(r_{ij}) = Cr_{ij}^{-12}$.

It is also instructive to consider the approximation

$$\langle \exp(-\beta\psi) \rangle \approx \exp(-\beta\bar{\psi}_a) \langle \exp(-\beta\psi_0) \rangle \tag{26}$$

required to make the mean field expression for $f(\Omega)$ consistent with the exact formal relation (19). As was noted in Section II, this is the most conservative approximation which will produce self-consistency; any approximation of the form

$$\langle \exp(-\beta\psi) \rangle \approx \exp(-\beta\bar{\psi}_a) \exp(-\beta\bar{\psi}'_0) \langle \exp(-\beta\psi''_0) \rangle \tag{27}$$

where $\psi_0 = \psi'_0 + \psi''_0$ are the orientation-independent terms in ψ, will serve the same purpose. Physically, (26) and (27) are tantamount to assuming that the translational structure of the fluid is determined by orientation-independent terms in the intermolecular pair potential, while the orientation-dependent interactions of one molecule with its neighbors merely provide a spatially uniform background potential $\bar{\psi}_a$, tending to align the molecule parallel to the director. If $\bar{\psi}''_0$ represents a sum of strong, very short-ranged repulsions, while $\psi'_0 + \psi_a$ represents a sum of weaker, longer-ranged attractions, this would seem to be a reasonable first approximation; in fact, it is conceptually equivalent to the approximation

$$\begin{aligned}\frac{\rho}{z} &= \langle\!\langle \exp(-\beta\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N))\rangle\!\rangle \\ &\approx \langle\!\langle \exp(-\beta\psi^*(\mathbf{r}_1,\ldots,\mathbf{r}_N))\rangle\!\rangle \exp(\beta\alpha\rho) \\ &= \frac{\rho}{z^*}\exp(\beta\alpha\rho)\end{aligned}$$

made by Longuet-Higgins and Widom[15] in their very successful van der Waals theory of simple liquids. (ψ^* and z^* are the one-body potential and activity in a fluid of hard spheres and α is a positive constant.) On the other hand, if the orientation dependence of the strong, very short-ranged intermolecular repulsions plays an important role in nematic systems and cannot be neglected, even to a first approximation, it would appear that (27) and the HJL type theory (with $\bar{\psi}_2$, $\bar{\psi}_4$, etc. proportional to ρ) to which it leads cannot readily be justified on molecular grounds. In this case, a more defensible use of the mean field approximation would be to replace the actual intermolecular repulsions by hard *rod* exclusions and approximate the effects of attractive interactions only by a pseudo-potential of the form $\bar{\psi}(\Omega) = W_0\rho + W_2\rho\eta P_2(\cos\theta) + W_4\rho\delta P_4(\cos\theta) + \cdots$. Two such calculations are reported elsewhere.[13,16]

Finally, since $\bar{\psi}_2 \propto \rho^4$ leads to statistical mechanical inconsistency and appears to be physically unrealistic as well, it is clear that the quantitative successes of the HJL theory cannot legitimately be used as evidence that nematic order results primarily from anisotropic dispersion forces.

References

1. For a discussion of this controversy, see A. Wulf, *J. Chem. Phys.*, **64**, 104 (1976), together with references 6, 13, and 16 below.
2. W. Maier and A. Saupe, *Z. Naturforsch.*, **14a**, 882 (1959); **15a**, 287 (1960).
3. R. L. Humphries, P. G. James, and G. R. Luckhurst, *Faraday Soc. Transactions II*, 1031 (1972).
4. R. L. Humphries and G. R. Luckhurst, *Chem. Phys. Lett.*, **17**, 514 (1972).
5. S. Chandrasekhar and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst.*, **24**, 179 (1973).
6. J. R. McColl and C. S. Shih, *Phys. Rev. Lett.*, **29**, 85 (1972).
7. As is customary, θ_i and ϕ_i are the polar and azimuthal angles, respectively, which specify the orientation of the cylindrical axis of a molecule with respect to a space-fixed coordinate system.
8. For a list of references to other mean field treatments of nematics, see S. Marcelja, *J. Chem. Phys.*, **60**, 3599 (1974).
9. Since the intermolecular pair potential should depend only on the *relative* orientations of two molecules, one must invoke some device such as an infinitesimal applied field in order to single out the "preferred" axis or director. In the absence of such a "symmetry-breaking" field (or some equivalent device), the orientational distribution function $f(\Omega)$ would be a constant in a nematic as well as an isotropic liquid.

10. B. Widom, *J. Chem. Phys.*, **39**, 2808 (1963).
11. See, for example, M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, *J. Math. Phys.*, **4**, 216 (1963); J. L. Lebowitz, G. Stell, and S. Baer, *J. Math. Phys.*, **6**, 1282 (1965); and reference 15 below.
12. See, for example T. L. Hill, *Statistical Mechanics*, (McGraw-Hill, New York, 1956), Chapter 7.
13. W. M. Gelbart and B. A. Baron, *J. Chem. Phys.*, in press.
14. M. A. Cotter, to be published.
15. H. C. Longuet-Higgins and B. Widom, *Mol. Phys.*, **8**, 549 (1964).
16. M. A. Cotter, *J. Chem. Phys.*, in press.