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Comments on the theory of dipolar fluids^{a)}

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In a recent article Chan, Mitchell, Ninham, and Pailthorpe¹ (CMNP) have re-examined certain aspects of the theory of dipolar fluids. I have several comments on Sec. II of this work.

CMNP find it useful to introduce a spherical cutoff into the dipole-dipole potential. Such a cutoff leads to manifestly well-defined integral expressions, and the advantages of its use have long been apparent.²⁻⁸ As CMNP point out, no such cutoff was used by Nienhuis and Deutch⁹⁻¹¹ (ND), and the ND integral expressions are consequently ambiguous if taken literally. The problem is that improper integrals involving the dipole tensor $\mathbf{T}(\mathbf{r}) = \nabla\nabla|\mathbf{r}|^{-1}$ are nonunique and hence do not exist mathematically. This is the "conditional convergence" problem to which CMNP allude, and which leads them to remark that the ND integral expressions require "very careful interpretation." This remark may unintentionally create the impression that unresolved subtleties are afoot. In fact, however, the origin and nature of the "conditional convergence" problem are well understood^{2,12,13} and the required interpretation is straightforward. A consistent interpretation of the ND expressions is obtained⁵ simply by replacing $\mathbf{T}(\mathbf{r})$ therein with

$$\mathbf{T}_{\text{ND}}(\mathbf{r}) = \mathbf{T}_\delta(\mathbf{r}) - (4\pi/3)\mathbf{U}\delta(\mathbf{r}), \quad (1)$$

where \mathbf{U} is the unit dyadic, $\delta(\mathbf{r})$ is the Dirac delta function, and $\mathbf{T}_\delta(\mathbf{r}) = H(|\mathbf{r}| - \delta)\nabla\nabla|\mathbf{r}|^{-1}$; here $H(x)$ is the Heaviside unit step function, and it is understood that the limit $\delta \rightarrow 0$ is ultimately to be taken. Equation (1) is a precise expression of the ND "singularity rule," given in Eq. (2.4) of Ref. 9.

Both $\mathbf{T}_\delta(\mathbf{r})$ and $\mathbf{T}_{\text{ND}}(\mathbf{r})$ may be manipulated formally as if they were nonsingular. It seems worthwhile to summarize some of their properties. The Maxwell electric field produced by a polarization $\mathbf{P}(\mathbf{r})$ is given by

$$\begin{aligned} \mathbf{E}(\mathbf{r}) &= -(4\pi/3)\mathbf{P}(\mathbf{r}) + \int d\mathbf{r}' \mathbf{T}_\delta(\mathbf{r} - \mathbf{r}') \cdot \mathbf{P}(\mathbf{r}') \\ &= \int d\mathbf{r}' \mathbf{T}_{\text{ND}}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{P}(\mathbf{r}'). \end{aligned} \quad (2)$$

Since $\nabla \cdot \mathbf{E}(\mathbf{r}) = -4\pi\nabla \cdot \mathbf{P}(\mathbf{r})$, it follows from Eq. (2) that $\nabla \cdot \mathbf{T}_\delta(\mathbf{r}) = -(8\pi/3)\nabla\delta(\mathbf{r})$, while $\nabla \cdot \mathbf{T}_{\text{ND}}(\mathbf{r}) = -4\pi\nabla\delta(\mathbf{r})$. Similarly, since $\nabla \times \mathbf{E}(\mathbf{r}) = 0$, we find that $\nabla \times \mathbf{T}_\delta(\mathbf{r}) = (4\pi/3)[\nabla\delta(\mathbf{r})] \times \mathbf{U}$, while $\nabla \times \mathbf{T}_{\text{ND}}(\mathbf{r}) = 0$. Among other things, these results are useful for deriving convolution relations. For example, the fact that $\mathbf{T}_{\text{ND}}(\mathbf{r})$ satisfies Eq. (3.31) of Ref. 9 is easily established by showing that both sides of the equation have the same divergence and curl.

The trace of $\mathbf{T}_\delta(\mathbf{r})$ is zero for all \mathbf{r} , while that of $\mathbf{T}_{\text{ND}}(\mathbf{r})$ is $-4\pi\delta(\mathbf{r})$. Thus the angular average of the di-

pole-dipole potential depends upon whether the latter is defined using $\mathbf{T}_\delta(\mathbf{r})$ or $\mathbf{T}_{\text{ND}}(\mathbf{r})$. If $\mathbf{T}_\delta(\mathbf{r})$ is used the average is zero for all \mathbf{r} , while if $\mathbf{T}_{\text{ND}}(\mathbf{r})$ is used the average contains a delta function at $\mathbf{r} = 0$.

The Fourier transform of $\mathbf{T}(\mathbf{r})$ is doubly nonunique, first because of the singularity at $\mathbf{r} = 0$, and second because it depends on the shape of the infinite volume over which the transform integral is taken. It is convenient to regard this infinite volume as spherical, a convention that appears to have been universally (but implicitly) adopted. The Fourier transforms of $\mathbf{T}_\delta(\mathbf{r})$ and $\mathbf{T}_{\text{ND}}(\mathbf{r})$ are then well defined, but of course are different. It is $\mathbf{T}_\delta(\mathbf{r})$ whose transform is given by Eq. (3.26) of CMNP; the transform of $\mathbf{T}_{\text{ND}}(\mathbf{r})$ then follows immediately from Eq. (1) above.

In the above discussion, the spherical cutoff distance δ ultimately tends to zero. CMNP, however, impose their spherical cutoff at a fixed finite distance r_0 , which is supposed to be small compared to the characteristic lengths over which the external field varies appreciably, but large compared to molecular dimensions. This second restriction on r_0 is entirely unnecessary,¹⁴ and deprives their derivation of much of its interest. If the limit $r_0 \rightarrow 0$ is taken, the form of the CMNP results is unchanged but their significance is greatly enhanced, since there is no longer any need to restrict attention to slowly varying external fields (provided that quadrupole and higher multipole interactions with the external field remain negligible). Equation (2.23) of CMNP (henceforth all equation numbers refer to CMNP) is valid in the limit $r_0 \rightarrow 0$, so that $\mathbf{E}_{\text{loc}}(\mathbf{r})$ is simply the Lorentz electric field.³ Equation (2.19) is therefore the exact microscopic constitutive relation between the polarization and the Lorentz electric field, valid even when these quantities vary rapidly with position.¹⁵ In the case of slowly varying fields, $\mathbf{P}(\mathbf{r})$ becomes locally proportional to $\mathbf{E}_{\text{loc}}(\mathbf{r})$; the dielectric constant ϵ then exists and is given by Eq. (2.26), which is a rearrangement of an earlier spherical-cutoff result due to Høye and Stell.⁶⁻⁸

If both \mathbf{r} and \mathbf{r}' are far from the walls (in a molecular sense) then the kernel in Eq. (2.19) depends only upon $(\mathbf{r} - \mathbf{r}')$ and the constitutive relation takes on the convolution form of Eq. (2.20). By Fourier transforming this equation, one can formally define a wave-vector-dependent dielectric tensor $\epsilon(\mathbf{k})$. This quantity is a tensor even in an isotropic fluid because of the physical distinction between transverse and longitudinal static polarization waves. Unfortunately, the concept of $\epsilon(\mathbf{k})$ is not useful in a finite sample, because the constitutive relation (2.20) then does not apply in all space and cannot be reduced to an algebraic relation by a Fourier transformation.

Although the exact constitutive relation (2.19) is of theoretical interest, its applicability is severely limited by the fact that *static* external fields with appreciable spatial variations on molecular length scales are rarely encountered. The only example that comes readily to mind is the field in the immediate vicinity of a test impurity of molecular size. Application of Eq. (2.19) to this case is unlikely to be fruitful, since this relation is a linear result which becomes invalid at high field strengths. In addition, the short-range correlation function h_0 will be modified by the presence of the impurity, and the evaluation of this modification would be more difficult than the direct evaluation of $P(r)$ from the impurity-dipole pair distribution function.

Finally, it must be emphasized that the short-range correlation function h_0 is *not* directly accessible via computer simulations as CMNP suggest. The problem is that h_0 is not the *complete* short-range part of the total correlation function $h^{(2)}$; the long-range part of the direct correlation function contributes to h at short range because of the convolution in the Ornstein-Zernike equation.

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¹D. Y. C. Chan, D. J. Mitchell, B. W. Ninham, and B. A.

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¹⁴CMNP imply that this restriction on r_0 is necessary for macroscopic electrostatics to be applicable, but this is not the case. For a given static external field, even one that varies rapidly with position, the statistical averaging defines a unique function $P(\mathbf{r})$. The electrostatic Maxwell equations [whose formal solution is Eq. (2)] then define the corresponding Maxwell electric field $\mathbf{E}(\mathbf{r})$. If the external field varies appreciably over distances of molecular magnitude then so will $P(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$, but both remain well defined.
¹⁵Unaware of the work of CMNP, I presented an independent derivation of this relation at the Fourth Annual West Coast Statistical Mechanics Conference (University of California, Los Angeles, June 6, 1978).

Reply to comments on the theory of dipolar fluids

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In a recent paper¹ we gave a derivation of the dielectric constant of a hard sphere dipole fluid which was needed as an intermediate result to obtain the Stillinger-Lovett condition and the Debye Hückel limiting law for ion-dipole mixtures. Ramshaw² has commented on this work and herein we reply.

To handle the long range part of the dipole-dipole potential we decomposed the direct correlation function into the sum of a short range term (which vanishes faster than r^{-3} as $r \rightarrow \infty$) and a term proportional to a cut off dipole-dipole potential. For $r > r_0$ this cutoff potential is just the familiar dipole-dipole potential, and for $r < r_0$ this potential vanishes. This procedure avoids the conditionally convergent integrals for $r \rightarrow 0$ which can arise later. Ramshaw² points out that it is possible to use the full dipole-dipole potential from r equal 0 to ∞ and furnishes a recipe for a consistent interpretation of the conditionally convergent integral. Our view is that in any reasonable model of dipolar fluids there are no divergencies at $r \sim 0$ from the dipole-dipole potential because the hard core part of the intermolecular potential will dominate. Therefore, it seems logical that

when trying to isolate the large distance properties of the dipole-dipole potential, one should not introduce an unnecessary conditional convergence at $r \sim 0$ especially when none is there in the first place. In the final analysis, it seems to us to be really a matter of personal preference to choose between a cutoff potential or to interpret an introduced conditional convergence.

In our paper we made the assumption that the cutoff distance r_0 should be sufficiently large for macroscopic electrostatics to be valid. Ramshaw points out that this restriction is unnecessary and that our result is more interesting than we first thought. We agree with his remarks and we thank him for pointing this out.

Our remarks on the accessibility of h_0 from machine calculations did have a fair degree of speculative content.

¹D. Y. C. Chan, D. J. Mitchell, B. W. Ninham, and B. A. Pailthorpe, *J. Chem. Phys.* **69**, 691 (1978).

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