Comment on "Local-Field Distribution in Random Dielectric Media"

In their Letter on the local-field distribution in dielectric media Sheng and Chen state two important conjectures concerning the correction term S to the Clausius-Mossotti formula for a random array in a lattice: (i) S is proportional to $\rho(1-\rho)$, where ρ is the average occupation of a site, and (ii) S is proportional to the mean-square deviation of the local-field distribution.[1] Both statements are motivated by numerical results obtained from a generalized Onsager approach applied to thousands of particles in a cavity. In this Comment we show analytically that the first conjecture is exact, while the second is rigorous to second order in the polarizability only. The only assumption we make is that fluctuations in the occupation of different sites are uncorrelated on the average, which is our definition of randomness. The proof is as follows. Let $\mathbf{E}_i=\mathbf{D}-\sum_j \overleftrightarrow{t}_{ij}\cdot\mathbf{p}_j$ be the local field at site i. Here $\mathbf{D}$ is the external field, $\overleftrightarrow{t}_{ij}$ the dipolar coupling tensor between sites i and j, and $\mathbf{p}_j=\rho_j\alpha\mathbf{E}_j$ the local dipole moment, where α is the particle polarizability, and $\rho_j=0,1$ the occupation number of site j. The fluctuation from the average field at a site $\langle\mathbf{E}_i\rangle=\mathbf{E}_m$ is then given by

$$\delta\mathbf{E}_i=-\alpha\sum_j \overleftrightarrow{t}_{ij}\cdot\delta\rho_j\mathbf{E}_m-\alpha\sum_j \overleftrightarrow{t}_{ij}\cdot(\rho_j\delta\mathbf{E}_j-\langle\rho_j\delta\mathbf{E}_j\rangle)\,. \quad (1)$$

The solution generated by iteration of this equation contains only terms that include the occupation number fluctuation $\delta\rho_k=\rho_k-\rho$ (k a site) as a factor. Since, in the above notation,[2] $S=\langle\rho_i\delta\mathbf{E}_i\rangle\cdot\mathbf{E}_m/\rho E_m^2$, evaluation of S involves averages of the form $\langle\rho_{k_1}\rho_{k_2}\cdots\rho_{k_{l-1}}(\rho_{k_l}-\rho)\rangle$. The assumption of uncorrelated fluctuations, stated as $\langle\delta\rho_{k_1}\delta\rho_{k_2}\delta\rho_{k_3}\cdots\delta\rho_{k_m}\rangle=0$, implies that the former average is zero unless k_n equals one of the other indices, in which case its value is $\rho^n(1-\rho)$, where n is the number of unequal sites involved. The minimal n that yields a nonzero average is 2 since $\langle\rho_{k_a}(\rho_{k_b}-\rho)\rangle$ matters when $k_a\neq k_b$ only ($\overleftrightarrow{t}_{aa}=0$). Thus S is of the form $\rho(1-\rho)P(\rho)$, where P is a polynomial with the constant term

$$P(0)=\sum_j \hat{\mathbf{z}}\cdot[(1+\alpha\overleftrightarrow{t}_{ij})^{-1}\overleftrightarrow{t}_{ij}\cdot\overleftrightarrow{t}_{ij}]\cdot\hat{\mathbf{z}}\,. \quad (2)$$

To lowest order in α one obtains for a cubic lattice $P(0)=16.8/d^6$, where d is the lattice constant. A comparison of these results with the corresponding data in Sheng and Chen[1] shows excellent agreement. This completes proof of conjecture (i).

To test (ii) we note that a single iteration of Eq. (1) permits writing

$$\delta\mathbf{E}_i=-\alpha\sum_j \overleftrightarrow{t}_{ij}\left[\delta\rho_j-\alpha\sum_{j'}\overleftrightarrow{t}_{jj'}[\rho_j(\rho_{j'}-\rho)-\langle\rho_j(\rho_{j'}-\rho)\rangle]\right]\cdot\mathbf{E}_m+O(\alpha^3) \quad (3)$$

from which follows to order α^2, $S=\alpha^2\rho(1-\rho)\sum_j\hat{\mathbf{z}}\cdot\overleftrightarrow{t}_{ij}\cdot\overleftrightarrow{t}_{ij}\cdot\hat{\mathbf{z}}$, where $\hat{\mathbf{z}}=\mathbf{E}_m/|\mathbf{E}_m|$. Also from Eq. (1) one obtains

$$\langle(\delta\mathbf{E}_i)^2\rangle=\alpha^2\sum_{jj'}\langle\delta\rho_j\delta\rho_{j'}\rangle\hat{\mathbf{z}}\cdot\overleftrightarrow{t}_{ij}\cdot\overleftrightarrow{t}_{ij'}\cdot\hat{\mathbf{z}}E_m^2+O(\alpha^3)\,.$$

Noting that $\langle\delta\rho_j\delta\rho_{j'}\rangle=\rho(1-\rho)\delta_{jj'}$ it follows to order α^2 that $S=\langle(\delta\mathbf{E}_i)^2\rangle/E_m^2$, which is just the mean-square deviation σ^2, also to second order in α. Conjecture (ii) therefore holds to this order of approximation. A similar procedure may be followed to compare terms in σ^2 and in S and one finds that already to order α^3 they are not the same. The conjecture is thus valid to second order in α only. This result is consistent with the data of Sheng and Chen[1] which support the conjecture at small values of α exclusively.

F. Claro
Facultad de Fisica
Pontificia Universidad Catolica de Chile
Casilla 6177, Santiago 22, Chile

G. D. Mahan
Department of Physics
University of Tennessee
Knoxville, Tennessee 37996
and
Solid State Division
Oak Ridge National Laboratories
Oak Ridge, Tennessee 37831

Received 19 November 1990
PACS numbers: 78.20.Dj, 41.10.−j, 42.20.−y, 77.20.+y

[1]Ping Sheng and Zhe Chen, Phys. Rev. Lett. **60**, 227 (1988).
[2]J. de Boer, F. van der Maesen, and C. A. Ten Seldam, Physica (Utrecht) **19**, 265 (1953).