Symmetry of the Dielectric Tensor

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In this note, I derive the symmetry of the dielectric tensor in two ways. The derivations are taken from Landau and Lifshitz's *Statistical Physics* [Second Revised edition, Pergamon, 1969] and *Electrodynamics of Continuous Media* [First edition, Pergaman, 1960]. The basic result is stated in ECM, sec. 76. There is a reference to SP, sec. 124. In the second edition, the corresponding references are actually to sec. 127. In contrast to their derivation, which is quantum mechanical and does not make direct use of Onsager's theorem, my first derivation uses Onsager's theorem and is classical. The direct use of Onsager's theorem assumes that the polarizability is a thermodynamic state variable, which is only true at low frequencies. A more general approach must use the fluctuation-dissipation theorem. Landau and Lifshitz's derivation of this theorem, based on classic papers by Callen and co-workers, makes the connection between time reversibility and the symmetry of the dielectric tensor a bit difficult to see. For that reason, I make use of a classical derivation that is given by Lenk [Phys. Lett., vol. 25A, no. 3, pp. 198–199, Aug. 14, 1967]. In another difference from Landau and Lifshitz, my derivations focus exclusively on the dielectric tensor. By contrast, Landau and Lifshitz apply a general result for any thermodynamic coefficient to the dielectric tensor. Finally, I focus on $\mathbf{P}$ as the dynamical variable, rather than $\mathbf{D}$, which makes it a little easier, in my view, to see what is going on. It also means that the Hamiltonian resembles more closely the quantum mechanical Hamiltonian.

The derivations proceed in four stages: (1) I first derive Onsager's theorem. (2) I next derive the appropriate conserved energy. (3) I derive the susceptibility tensor from Onsager's kinetic coefficients, and I show that this tensor and, consequently, the dielectric tensor are symmetric. (4) Finally, I derive the fluctuation-dissipation theorem in its classical form and use it to demonstrate the symmetry of the dielectric tensor.

I. Onsager's Theorem

The entropy will be a function of the internal energy and the other state variables of the system. Hence, we may write $S = S(U, P_j)$, where S is entropy, U is internal energy, and P_j is the polarizability, which we will assume is constant over the medium. All other state variables (pressure, temperature, and so on) are assumed to be constant. We will use Einstein notation throughout, so that P_j is another way of writing $\mathbf{P}$, P_jE_j is the same as $\mathbf{P}\cdot\mathbf{E}$, $\partial X/\partial P_j$ is the same as $\nabla_{\mathbf{P}}X$, and so on. At thermodynamic equilibrium, the entropy must be a maximum, so that $\partial S/\partial P_j = 0$ and $\partial^2 S/\partial P_j \partial P_k < 0$. Due to fluctuations, the medium will not be exactly at thermal equilibrium, in which case $R_j = -\partial S/\partial P_j \neq 0$. Assuming that the system is closed, then we must be able to write

$$R_j = \beta_{jk} P_k, \tag{1}$$

We now find,

$$\frac{\partial R_j}{\partial P_k} = \beta_{jk} = -\frac{\partial^2 S}{\partial P_j \partial P_k} = \beta_{kj}, \tag{2}$$

so that the tensor $\beta \equiv \beta_{jk}$ is symmetric. Explicitly, we have for the entropy, $S - S_0 = -(1/2)\beta_{jk}P_jP_k$, where S_0 is the entropy at thermodynamic equilibrium, so that the probability distribution function for the P_j may be written

$$w(P_j) = \frac{\sqrt{\det \beta}}{(2\pi)^{3/2}} \exp\left[-\frac{1}{2}\beta_{jk}P_jP_k\right]. \tag{3}$$

To obtain, Eq. (3), we use the fundamental assumption of statistical mechanics that the probability distribution function of the macroscopic state variables P_j may be written $w(P_j) \propto \exp[S(P_j)]$, and we may assume that the fluctuations are small, so that cubic and higher-order terms in the expansion $S - S_0$ are negligible. Using this probability distribution function to obtain the average value of the product P_jR_k, we find

$$\overline{P_jR_k} = \frac{\sqrt{\det \beta}}{(2\pi)^{3/2}} \int P_j\beta_{kl}P_l \exp\left[-\frac{1}{2}P_l\beta_{lm}P_m\right] d^3P = \delta_{jk}, \tag{4}$$

where δ_{jk} is the Kroenecker delta function (identity tensor).

When a fluctuation occurs that is large compared to the mean fluctuation, but small compared to the value at which the system would behave nonlinearly, we may write

$$\dot{P}_j = \dot{P}_j(P_1, P_2, P_3) = -\lambda_{jk}P_k. \tag{5}$$

In the same regime, it must be possible to write

$$\dot{P}_j = -\gamma_{jk}R_k. \tag{6}$$

The γ_{jk} are referred to as kinetic coefficients, and Onsager's theorem states that $\gamma_{jk} = \gamma_{kj}$, as long as the microscopic dynamics is time reversible. If there is a rotation or a magnetic field, then the sign of the rotation or the magnetic field must be reversed to make the dynamics time reversible. So, the statement of the theorem is $\gamma_{jk}(\mathbf{H}) = \gamma_{kj}(-\mathbf{H})$.

To prove this result, we write

$$\begin{aligned} \overline{P_j(t)P_k(t+\tau)} &= \overline{P_j(t-\tau)P_k(t)} \qquad \text{(homogeneity of time)} \\ &= \overline{P_j(t+\tau)P_k(t)}. \qquad \text{(microscopic reversibility)} \end{aligned} \tag{7}$$

We then take the derivative with respect to τ and set $\tau = 0$ to obtain

$$\overline{P_j(t)\dot{P}_k(t)} = \overline{\dot{P}_j(t)P_k(t)}. \tag{8}$$

Substitution of Eq. (6) into Eq. (8) and using the relation $\overline{P_jR_k} = \delta_{jk}$ that we derived in Eq. (4), we finally obtain Onsager's theorem: $\gamma_{jk} = \gamma_{kj}$.

II. Energy and Entropy of a Dielectric Medium in an Oscillating External Electric Field

We imagine now that our dielectric medium is placed in a sinusoidally oscillating electric field,

$$E_j(t) = \frac{1}{2}E_{0j}\exp(-i\omega t) + \frac{1}{2}E^*_{0j}\exp(i\omega t), \tag{9}$$

which may be created, for example, by placing a slab of our dielectric material between the plates of a capacitor, and using an oscillating voltage source with a fixed voltage.

The Hamiltonian for the system may be written

$$H(p_\alpha, x_\alpha) = H_0(p_\alpha, x_\alpha) - \epsilon_0 V P_j E_j(t), \tag{10}$$

where V is the volume of the dielectric material, ϵ_0 is the vacuum permittivity, the p_α and x_α are the momenta and coordinates of the microscopic constituents, and $P_j = e_\alpha x_{\alpha j}$, where the e_α are the charges corresponding to the x_α. A point to note is that the particle locations will change due to the external electrical field, so that the total energy due to the polarizability will be $-(1/2)\epsilon_0 V P_j E_j$, assuming that the polarizability is linearly proportional to the electric field. As a consequence, H_0 must contribute an amount $+(1/2)\epsilon_0 V P_j E_j$ to the total field energy. At the same time, H_0 must be constant. Hence, the energy that goes into the field from H_0 must be compensated by a decrease in the entropy of the dielectric material. Physically, the separation of charges creates a more ordered system. This decrease in the dielectric's entropy does not violate the second law, since the entropy of the external source will increase.

Using the relationship $dU(S, P_j)/dt = \partial H/\partial t$, we conclude that

$$dU = TdS - \epsilon_0 V \overline{P_j} dE_j, \tag{11}$$

where where $\overline{P_j}$ is the equilibrium polarizability at each point in time. Writing $U_0 = U + \epsilon_0 V P_j E_j(t)$, we find that

$$dU_0 = TdS + \epsilon_0 V E_j d\overline{P_j}. \tag{12}$$

Since U_0 is constant, we conclude that

$$\overline{R_k} = -\left.\frac{\partial S}{\partial \overline{P_j}}\right|_{U_0} = \frac{1}{T}\epsilon_0 E_j, \tag{13}$$

where $\overline{R_k}$ is the equilibrium value of R_k.

III. Onsager's Theorem and the Symmetry of the Dielectric Tensor

We will assume that the oscillating field is sufficiently small that β_{jk} and γ_{jk} are unchanged by the oscillating field. Another key assumption is that the oscillation is sufficiently slow that the system is at its equilibrium — except for fluctuations — at each point in time. Strictly speaking, this assumption will only be true at frequencies that are lower than the lowest resonances in the dielectric material. That assumption will not be true at optical frequencies. In effect, the $\dot{P}_j$ are not only functions of the P_j. Landau and Lifshitz show how to take this issue into account using a full quantum-mechanical calculation. One could also take it into account with a classical calculation in which the variable set is enlarged to include one polarizability function and its first-derivative in time for each resonance.

As a consequence of the oscillatory electric field, the polarizability will have an offset, so that

$$\dot{P}_j = -\gamma_{jk}(R_k - \overline{R_k}) = -\gamma_{jk} R_k - \frac{1}{T}\epsilon_0 \gamma_{jk} E_k. \tag{14}$$

Defining now the susceptibility tensor by analogy to Eq. (9),

$$P_j(t) = \frac{1}{2}\epsilon_0 \chi_{jk}(\omega) E_0 \exp(-i\omega t) + \frac{1}{2}\epsilon_0 \chi^*_{jk}(\omega) E^*_0 \exp(i\omega t), \tag{15}$$

and substituting into Eq. (14), we find

$$i\omega\epsilon_0\chi_{jm}(\omega) = \gamma_{jk}\beta_{kl}\epsilon_0\chi_{lm}(\omega) - \frac{1}{T}\gamma_{jm}. \tag{16}$$

Solving for $\chi_{jk}(\omega)$, we find

$$\epsilon_0\chi_{jk}(\omega) = \frac{1}{T}(\beta - i\omega\gamma^{-1})^{-1}_{jk}, \tag{17}$$

where β and γ indicate the matrices corresponding to β_{jk} and γ_{jk} and the superscript -1 indicates the matrix inverse. From the symmetry properties of β and γ, it follows immediately that $\chi_{jk}(\omega, \mathbf{H}) = \chi_{kj}(\omega, -\mathbf{H})$.

We conclude that

$$\epsilon_{jk} = \epsilon_0(\delta_{jk} + \chi_{jk}) \tag{18}$$

obeys the relation

$$\epsilon_{jk}(\omega, \mathbf{H}) = \epsilon_{kj}(\omega, -\mathbf{H}). \tag{19}$$

IV. The Fluctuation-Dissipation Theorem and the Symmetry of the Dielectric Tensor

Our starting point is to note that we may write

$$\overline{P_j(t)P_k(t+\tau)} = \overline{P_j(t)\Xi_{jk}(\tau)}, \tag{20}$$

where $\Xi_{jk}(\tau) = \overline{P_k(t+\tau)|P_j(t)}$. We define the covariance

$$\Phi_{jk}(\tau) = \overline{P_j(t)P_k(t+\tau)} = \overline{P_j(t)\Xi_{jk}(\tau)}, \tag{21}$$

and the corresponding power spectrum,

$$S(\omega) = \int_{-\infty}^{\infty} \Phi_{jk}(\tau) \exp(i\omega\tau)\, d\tau. \tag{22}$$

We now write explicitly

$$\Phi_{jk}(\tau) = \int w_0(P_j) P_j \Xi_{jk}(\tau) d^3P, \tag{23}$$

where $w_0(P_j)$ is the distribution function for the P_j at equilibrium.

We now consider an energy perturbation $-\epsilon_0 V P_k(t) E_k(t)$, where $E_k(t)$ is the imposed electric field. We will take

$$E_k(t) = E_{k0}, \text{ when } t < 0, \qquad \text{and} \qquad E_k(t) = 0, \text{ when } t > 0. \tag{24}$$

The equilibrium probability density when $t < 0$ is given by

$$w(P_k) = w_0(P_k) \exp\left(\epsilon_0 V P_k E_{k0}/k_\mathrm{B}T\right), \tag{25}$$

where k_B is Boltzmann's constant. When $t > 0$, the relation process is governed by $\Xi_{jk}(\tau)$, so that the mean value of $P_j(t)$ is given by

$$\overline{P_k(t)} = \int w(P_j) \Xi_{jk}(t)\, d^3P = \frac{\overline{\exp(\epsilon_0 V P_j E_{j0}/k_\mathrm{B}T) \Xi_{jk}(t)}}{\overline{\exp(\epsilon_0 V P_j E_{j0}/k_\mathrm{B}T)}}. \tag{26}$$

We may also write

$$\overline{P_k(t)} = \epsilon_0 \int_0^\infty X_{jk}(\tau) E_j(t-\tau)\, d\tau, \tag{27}$$

which becomes in our case

$$\overline{P_k(t)} = E_{j0} \int_t^\infty X_{jk}(\tau)\, d\tau. \tag{28}$$

Assuming that $|\epsilon_0 V P_j(t) E_j(t)| \ll k_\mathrm{B}T$, we may expand the exponential functions in Eq. (26), keeping only first-order contributions in powers of E_{j0}. We then find

$$\overline{P_k(t)} = \frac{\epsilon_0 V E_{j0}}{k_\mathrm{B}T} \overline{P_j(0) P_k(t)} = \frac{\epsilon_0 V E_{j0}}{k_\mathrm{B}T} \Phi(t). \tag{29}$$

We conclude

$$\Phi_{jk}(t) = \frac{k_\mathrm{B}T}{V} \int_t^\infty X_{jk}(\tau)\, d\tau. \tag{30}$$

We now take the Fourier transform of both sides, noting that $\Phi_{jk}(t) = \Phi_{ij}(-t)$. We then obtain

$$\begin{aligned} S_{ij}(\omega) &= -i \frac{k_\mathrm{B}T}{\omega V} [\chi_{jk}(\omega) - \chi^*_{jk}(\omega)] \\ &= 2 \frac{k_\mathrm{B}T}{\omega V} \operatorname{Im}[\chi_{jk}(\omega)]. \end{aligned} \tag{31}$$

Equation (31) is the classical form of the fluctuation-dissipation theorem.

We now invoke the symmetry of $\Phi_{jk}(\tau)$ under time reversal to write $S_{jk}(\omega, \mathbf{H}) = S_{kj}(\omega, -\mathbf{H})$, just as in the previous section. As a consequence, we find $\operatorname{Im}[\chi_{jk}(\omega, \mathbf{H})] = \operatorname{Im}[\chi_{kj}(\omega, -\mathbf{H})]$. From the Kramers-Kronig relations, we now infer $\operatorname{Re}[\chi_{jk}(\omega, \mathbf{H})] = \operatorname{Re}[\chi_{kj}(\omega, -\mathbf{H})]$. Putting these two pieces together, we find $\chi_{jk}(\omega, \mathbf{H}) = \chi_{kj}(\omega, -\mathbf{H})$, from which the final result,

$$\epsilon_{jk}(\omega, \mathbf{H}) = \epsilon_{kj}(\omega, -\mathbf{H}) \tag{32}$$

follows.