# On an admissible sign of the static dielectric function of matter

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This paper is a review of the present status of the problem of the properties of the dielectric function of matter. It is shown that the dielectric function $\epsilon(\mathbf{q},\omega)$ obeys the Kramers–Kronig relations only when momentum $\mathbf{q}$ is identically equal to zero. For an arbitrary momentum $\mathbf{q}\neq 0$ the dielectric function does not obey the Kramers–Kronig relations, and the static dielectric function at $\mathbf{q}\neq 0$ may have a negative sign $[\epsilon(\mathbf{q},0)<0]$. It is shown that the appearance of a negative sign for the static dielectric function does not contradict the requirements of system stability. Special attention is paid to the possible existence of a negative sign for the static dielectric function in real physical systems. It is shown that the inequality $\epsilon(\mathbf{q},0)<0$ at $\mathbf{q}\neq 0$ is valid for a rather wide class of condensed media (simple metals, nonideal plasma, etc.). The interrelation between the existence of a negative sign for the dielectric function and the problem of high-temperature superconductivity is briefly discussed.

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## I. INTRODUCTION

There is some question whether the longitudinal static dielectric function (DF) of matter $\varepsilon(\mathbf{q},\omega)$ at $\omega=0$ can acquire negative values. This question is first of all of general physical interest, since it associates the existence of general model-independent limitations upon such an important characteristic of matter as DF with the conditions of causality, stability, etc. It is also important in particular cases, for example, in the problem of a radical increase of the superconductor critical temperature $T_c$: from the condition $\varepsilon(\mathbf{q},0)>0$ a rather rigid and universal upper bound on the value of $T_c$ has been derived (Cohen and Anderson, 1972).[1]

Most guides to the electrodynamics of condensed media give an unreservedly negative answer to this question. Such a conclusion follows directly from the Kramers–Kronig relations for the DF, which undoubtedly contradict the negative sign of the DF. However, the very problem of the existence of Kramers–Kronig relations discussed in many papers (Landau and Lifshitz, 1960; Pines and Nozières, 1966; Martin, 1967; Kirzhnits, 1976) turns out to be not at all simple.

Almost fifteen years ago Pines and Nozières (1966) emphasized that Kramers–Kronig relations for the DF $\varepsilon(\mathbf{q},\omega)$ itself cannot be derived from the causality principle, since this quantity is a function of response to the *total* field, which in the general case cannot be controlled. Control can be realized for an external field only; and, correspondingly, Kramers–Kronig relations can be derived from the causality principle only for the inverse DF $\varepsilon^{-1}(\mathbf{q},\omega)$, which serves as a function of response to an *external* field. However, an apprehension was expressed in the same book that with the violation of Kramers–Kronig relations for the DF there arises an instability under a spontaneous appearance of a positively charged density wave.

The view that violation of Kramers–Kronig relations for the DF is nevertheless possible and in some cases even inevitable was expressed by Martin (1967). The author gives an example of a physical situation (a uniform electron gas near the crystallization point) in which Kramers–Kronig relations are violated already in the stable phase near the values of a momentum which correspond to the lattice parameter of the crystal. Unfortunately, the question of the sign of the DF was not investigated in this work at all, and the problem of stability was only mentioned.

The most detailed and systematic investigation of this problem has been carried out by one of the present authors (Kirzhnits, 1976), who was stimulated by studies on high-temperature superconductivity [see also Kirzhnits (1977)]. This work analyzes the need to fulfill both Kramers–Kronig relations and stability conditions and shows that at any nonzero wave vectors $\mathbf{q}$ the DF of matter is not really obliged to obey Kramers-Kronig relations. Consequently, the quantity $\varepsilon(\mathbf{q},0)$ can be negative without any contradiction of causality and stability requirements. However, as is established in the same book, at $q\to 0$ Kramers–Kronig relations must be satisfied both for the DF itself and for its reciprocal. Correspondingly, the long-wave limit of the static DF must be a positive quantity. It is only to this case that the general statement made by Landau and Lifshitz (1960) on the necessity of a positive sign of DF refers.

[1]See the appendix also.


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At the same time, the work by Kirzhnits (1976) left practically untouched the question of the existence of real media with a negative static DF. Moreover, the author expressed the opinion that such systems, if they do exist, must be rather exotic ones. In recent years the situation has changed radically [see Fasolino *et al.* (1978), Dolgov and Maksimov (1978), and Hansen and McDonald (1978)]. The inequality $\varepsilon(\mathbf{q},0)<0$ at $\mathbf{q}\neq 0$ has turned out to be fulfilled for a rather wide class of condensed media (simple metals, nonideal plasma, etc.). These facts are unfortunately not yet generally known, and up to now there have appeared some papers based on the use of too strict an inequality $\varepsilon(\mathbf{q},0)>0$ (Cohen, 1979; Rajogopal, 1979).[2]

The main aim of the present review, therefore, to present systematically the status of the problem of an admissible sign of the static DF and to consider certain examples of real physical systems with a negative value of $\varepsilon(\mathbf{q},0)$. For a more detailed consideration of this problem see the preprint by Dolgov *et al.* (1978).

In this paper we use the units $\hbar=1$, $k=1$.

## II. DIELECTRIC FUNCTION OF HOMOGENEOUS SYSTEMS

### A. A general theoretical consideration

Let us first of all define the quantity $\varepsilon(\mathbf{q},\omega)$, understanding it as a longitudinal DF of a homogeneous and isotropic substance.[3] We shall subject the system under consideration to the action of an external source with the Fourier component of the charge density $\delta\rho_e(\mathbf{q},\omega)$. As a result there appears in the system an induced charge $\delta\rho_i(\mathbf{q},\omega)$, which together with $\delta\rho_e$ makes up the total change in the charge density $\delta\rho_t=\delta\rho_e+\delta\rho_i$. The corresponding values of the induction $\delta\mathbf{D}$ and the field strength $\delta E$ are determined from the Maxwell equations[4]:

$$\operatorname{div}\delta\mathbf{D}=4\pi\delta\rho_e,\quad \operatorname{div}\delta\mathbf{E}=4\pi\delta\rho_t\,. \tag{1}$$

In the language of introduced values DF is defined by either of the following relations:

$$\begin{aligned}\delta\mathbf{D}(\mathbf{q},\omega)&=\varepsilon(\mathbf{q},\omega)\delta\mathbf{E}(\mathbf{q},\omega)\,,\\ \delta\rho_e(\mathbf{q},\omega)&=\varepsilon(\mathbf{q},\omega)\delta\rho_t(\mathbf{q},\omega)\,.\end{aligned} \tag{2}$$

In what follows we shall use for convenience either the variables $\delta\mathbf{D}$, $\delta\mathbf{E}$ or $\delta\rho_e$, $\delta\rho_t$.

To clarify the question of admissible sign for the static DF of matter one can use two types of arguments based, respectively, on causality and system stability considerations. These arguments, which are closely connected with each other, will be considered below.

#### 1. Causality (Kramers-Kronig relations)

If one imposes some influence ($I$) on the system under consideration and examines the change ($A$) which it induces, one can introduce a response function ($R$) by the relation

$$A=R\times I\,. \tag{3}$$

The causality principle requires that the change be delayed with respect to the influence itself. This imposes definite and well known limitations on the analytical properties of the response $R$ as a function of frequency, which are expressed by relations of the Kramers–Kronig type,

$$R(\mathbf{q},\omega)=R(\mathbf{q},\infty)+\frac{1}{\pi}\int_0^\infty\frac{d\omega'^2\,\operatorname{Im}R(\mathbf{q},\omega')}{\omega'^2-\omega^2-i\delta}\,. \tag{4}$$

In the static limit

$$R(\mathbf{q},0)=R(\mathbf{q},\infty)+\frac{1}{\pi}\int_0^\infty\frac{d\omega'^2}{\omega'^2}\operatorname{Im}R(\mathbf{q},\omega')\,. \tag{4'}$$

Limitations on the value and sign of the static DF will be found from the latter relation.

With this purpose it should be clarified whether the DF [and reciprocal to it $1/\varepsilon(\mathbf{q},\omega)$] can be treated as a response function. The simplest case is when we act on the system by an external charge ($I=\delta\rho_e$) and consider the full change in the charge ($A=\delta\rho_t$) to be the result of this action. Then according to Eq. (3) the function ($R=1/\varepsilon$) reciprocal to DF will serve as a response function, and one can write Kramers–Kronig relations for it. With account taken of the equality $\varepsilon(\mathbf{q},\infty)=1$, Eq. (4) gives

$$1/\varepsilon(\mathbf{q},0)=1+\frac{1}{\pi}\int_0^\infty\frac{d\omega'^2}{\omega'^2}\operatorname{Im}1/\varepsilon(\mathbf{q},\omega')\,. \tag{5}$$

If we also take into account the inequalities

$$\operatorname{Im}\varepsilon(\mathbf{q},\omega)\geqslant 0,\quad \operatorname{Im}1/\varepsilon(\mathbf{q},\omega)\leqslant 0\,, \tag{6}$$

following from a direct relation of the quantity $\operatorname{Im}1/\varepsilon(\mathbf{q},\omega)$ with the structure factor of the system (or with the probability of an inelastic particle scattering on the system), then inequalities of the form $1/\varepsilon(\mathbf{q},0)\leqslant 1$ or, equivalently,

$$\varepsilon(\mathbf{q},0)\geqslant 1,\quad \varepsilon(\mathbf{q},0)<0 \tag{7}$$

follow directly from Eq. (5). Thus the causality conditions corresponding to the action of an external charge on the system do not preclude negative values for a static DF system. Only the values between 0 and 1 turn out to be forbidden.

It is instructive to note that one can in principle realize the influence of an external charge with any arbitrary values of the wave vector $\mathbf{q}$; correspondingly, the inequalities (7) hold for arbitrary values of this quantity. In fact, an external charge with $\mathbf{q}=0$[5] is easily directed by placing the system inside a capacitor on which the external charge density changes. As for the case $\mathbf{q}\neq 0$, it is easily realized if we imagine within the system a conductor with a small external point charge having a large mass and hence not subject to the influence of the system. The field of this charge has all the Fourier components.

[2]As is shown in Sec. III of the present review, the Wigner crystal DF considered in these papers is actually negative.

[3]In Sec. III the case of an anisotropic inhomogeneous substance (crystalline medium) will be considered in detail.

[4]We should emphasize that here and below the quantity $\mathbf{E}$ designates a real microscopic field, but not a field averaged over a physically infinitesimal volume.

[5]More precisely, with $q\sim L^{-1}$, where $L$ is the characteristic length of the system.

Let us pass to the second case, in which the influence is imposed not by an external but by a total charge ($I = \delta\rho_t$) and the induced change is a variation in the external charge ($A = \delta\rho_e$). In this case, which is much more complicated than the previous one, the response function is the DF itself [$R = \varepsilon(q,\omega)$, see Eq. (2)]. If the letter quantity could really be thought of as a response function, the Kramers–Kronig relations (4) would hold for it—in particular, relation (4′):

$$\varepsilon(\mathbf{q},0) = 1 + \frac{1}{\pi}\int_0^\infty \frac{d\omega'^2}{\omega'^2}\,\mathrm{Im}\,\varepsilon(\mathbf{q},\omega')\,. \tag{8}$$

By virtue of the same inequalities (6), from this relation it would follow that a negative value for the static DF $\varepsilon(\mathbf{q},0) \geq 1$ is impossible. Therefore, to decide whether such values are possible one must determine whether the DF may be considered at arbitrary momenta as a response function. This appears to be possible only for $\mathbf{q} = 0$ (more precisely for $\mathbf{q} \sim 1/L$).

So, the Kramers–Kronig relations for the DF itself can be written for $\mathbf{q} = 0$ only, and then Eq. (8) gives the inequality[6]

$$\varepsilon(\mathbf{q}=0,0) \geq 1\,, \tag{9}$$

which is usually presented without the condition that it is valid for a long-wave limit only.

To confirm what has been said one should bear in mind that the very nature of the total charge (or the field strength $\mathbf{E}$) is such that it is much more difficult to govern the behavior of these quantities than that of the external charge or of induction. In any case this can be done by placing the system inside a capacitor on which it is not the charge density as before but the potential difference that changes according to the law assumed. By changing the latter quantity with the aid of a battery we change the field strength (the total charge), and the external charge flowing to (or away from) the capacitor characterizes the result of such an action. It is obvious that in the imaginary experiment under consideration only the Fourier components of the charge or field with $\mathbf{q} = 0$.

Any attempt to fix an arbitrary Fourier component of the total charge or field strength is in principle condemned to failure. If, for example, one introduces into the system a conductor on the end of which an electrostatic potential is kept (or changed according to the given law), this fixes the field strength only in the immediate neighborhood of the end of the conductor. At other points of the system the values of the strength cannot be considered given since they are determined by the response of the system. Meanwhile, the Fourier component of the strength depends on the values of this quantity in the entire space. A successful result might be achieved only by placing inside the system a set of conductors, the potential at the ends of which is fixed or changes according to the given law. The higher the value of $\mathbf{q}$, the denser this set must be. It is clear, however, that we shall be dealing here with a system which has nothing in common with the original one.

## 2. Stability

The above results are confirmed by considerations having to do with the stability of the system. Inequalities (7) and (9) acquire the physical meaning of stability criteria.

Let us ask what will happen to the system when the Kramers–Kronig relations are violated. It is readily seen that in this case the system will be unstable under a spontaneous appearance of an electric field (if the relation for $1/\varepsilon$ is violated) or induction (if the relation for the DF itself is violated). This can be seen from the fact that the Kramers–Kronig relations express the analyticity of the corresponding functions in a complex frequency plane. Therefore a violation of these relations will lead to the appearance of a zero or a pole for DF, respectively, at a complex value of frequency. As can be seen from Eq. (2), this will mean an increase in time of the field strength $\mathbf{E}$ or induction $\mathbf{D}$.[7]

It is instructive to note that in a system taken by itself (in the absence of external charges) the induction that appears spontaneously must satisfy the Maxwell equation $\mathrm{div}\,\delta\mathbf{D} = 0$ [see Eq. (1)]. It follows from this that the corresponding instability appears only at $\mathbf{q} = 0$, due to the equation $\mathbf{q}\cdot\delta\mathbf{D}(\mathbf{q},\omega) = 0$. At the same time a spontaneously appearing field strength which satisfies the equation $\mathrm{div}\,\delta\mathbf{E} = 4\pi\delta\rho_i$ may have arbitrary Fourier components. What has been said makes it clearer why condition (9) refers to $\mathbf{q} = 0$ only, whereas condition (7) refers to arbitrary $\mathbf{q}$.

For a consistent consideration of stability under a spontaneous appearance of some quantity $\varphi$ one should introduce the so-called effective potential $V(\varphi)$, which corresponds in the simplest cases to the energy or free energy and has a minimum in $\varphi$ when in equilibrium. The conditions for the minimum of this quantity give the criterion of stability. It is known that there exists a relation $\partial V(\varphi)/\partial\varphi = -j$, where $j$ is a current conjugate to the quantity $\varphi$ (the interaction has the form $j\varphi$). From this the system stability conditions take the form

$$\frac{\partial V(\varphi)}{\partial\varphi} = -j = 0, \quad \frac{\partial^2 V(\varphi)}{\partial\varphi^2} = -\frac{\partial j}{\partial\varphi} \geq 0\,, \tag{10}$$

where the quantities $\varphi$ and $j$ belong to a definite value of $q$ and $\omega = 0$.

To consider uniformly both the above-mentioned cases, i.e., the appearance of the field $\mathbf{E}$ and induction $\mathbf{D}$, it is convenient to choose for the quantity $\varphi$ the medium polarization

$$\mathbf{P} = \frac{\mathbf{D}-\mathbf{E}}{4\pi}, \quad \mathrm{div}\mathbf{P} = -\rho_i$$

and for the current the corresponding external field $-\mathbf{D}$ and $-\mathbf{E}$. Then conditions (10) give the inequalities (7) and (9), which thus play the role of system stability criteria. Note that the same inequalities could be

[6]Note that as the inequality (9) is violated in a one-component charged system with a homogeneous compensating background, the compressibility of the system becomes negative, which leads to the instability of the system. This is an additional argument in favor of Eq. (9) [see Pines and Nozières (1966)].

[7]In these considerations it is sufficient to limit ourselves to the case when the DF remains real at $\omega = 0$. Then the frequency acquires an imaginary part of both the signs, one of which corresponds certainly to the increase of the corresponding quantity.

directly observed from the Le Chatelier-Braun principle: The response of the system to the action from outside must be a weakened resistance to this action. In our case the response of the system consists in the appearance of the charge $\delta\rho_i$ equal to

$$(\varepsilon^{-1}-1)\delta\rho_e=(1-\varepsilon)\delta\rho_t\,. \tag{11}$$

Requiring that this quantity diminish $\delta\rho_e$ and $\delta\rho_t$, respectively, we come indeed to the inequalities (7) and (9). From the relations presented above one can find expressions for the effective potential with respect to the field $\mathbf{E}$ and induction

$$V(\mathbf{E})=\frac{\varepsilon(\varepsilon-1)}{8\pi}E^2,\quad V(\mathbf{D})=\frac{\varepsilon-1}{8\pi\varepsilon^2}D^2\,. \tag{12}$$

These expressions are far from coinciding with the total energy of a polarized system:

$$\frac{\varepsilon E^2}{8\pi}=\frac{D^2}{8\pi\varepsilon}\,. \tag{13}$$

So, the potential $V(\mathbf{E})$ is obtained from the total energy $D^2/8\pi\varepsilon$ by Legendre transformation to the variable $E$ (this gives $-\varepsilon E^2/8\pi$) and also by a further subtraction of energy $D^2/8\pi$, which would, in a vacuum, come from the external sources (in this case from the external charge $\rho_e$). For this reason the arguments in favor of a positive sign for the *DF* based on Eq. (13) cannot be considered correct.

Concluding this section we should note that a violation of condition (7) at $\mathbf{q}\neq 0$ leads to the spontaneous appearance in the system of charge density waves with a given value of $\mathbf{q}$. This follows directly from what has been said above: Violation of condition (9) implies violation of the stability criterion by a spontaneous appearance of polarization or, equivalently, an induced charge $\rho_i$.

### B. Physical examples

In the preceding section we have shown that the existence of negative values for a static longitudinal DF does not contradict the general principles of electrodynamics of condensed matter and does not lead to instability of the system. This fact by itself does not mean, of course, that such a situation is sure to occur in concrete systems. It appears, however, that the existence of negative values for a static DF is not only possible but in some important cases inevitable. In what follows it will be seen that examples of such systems are already being considered in the literature.

We shall concern ourselves with the simplest model system, namely, that of charged one-component plasma electrons on a homogeneous compensating background. This model has lately attracted much attention and has been studied intensively both in the quantum case and in the classical limit.

#### 1. Electron quantum plasma

The interest in quantum one-component plasma [see Lundqvist (1973), Brovman and Kagan (1974), Kugler (1975), and Gorobchenko and Maksimov (1980)] is first of all due to the fact that this model renders rather well a large number of characteristic properties of electrons in metals. Neglecting exchange and correlation effects, the corresponding expression for the DF has the form

$$\varepsilon(\mathbf{q},0)=1-\frac{4\pi e^2}{q^2}\pi_0(\mathbf{q},0)\,, \tag{14}$$

where

$$\pi_0(\mathbf{q},0)=-N(0)\left(1+\frac{1-x^2}{2x}\ln\left|\frac{1+x}{1-x}\right|\right),\quad x=q/2P_F$$

is a polarization operator of the noninteracting electron gas (Lindhart, 1954), and where $N(0)$ is an electron state density on the Fermi surface. The quantity $\pi_0(\mathbf{q},0)$ is seen to be negative at all values of the momentum $\mathbf{q}$. Therefore, when exchange and correlation effects are disregarded, the static DF of the electron gas is decidedly a positive quantity.

So it is clear that we may hope to obtain a negative value for the DF in an electron gas only if exchange and correlation effects play an essential role. The relative magnitude of these effects is determined by dimensionless parameters

$$r_S=\left(\frac{3n}{4\pi a_B^3}\right)^{1/3},$$

where $n$ is the electron density, and $a_B=1/me^2$ is the Bohr electron radius. The quantity $r_S$ in practice represents the ratio of the potential energy of particles to their mean kinetic energy. In a strongly compressed system, where $r_S\ll 1$, all the exchange and correlation effects can be fully disregarded, and Eq. (14) will be valid for the DF. In a system with low density, where $r_S\gg 1$, the exchange and correlation effects must be taken into account. The electron plasma of real metals possesses densities in an intermediate region $1\lesssim r_S\lesssim 6$, and therefore the calculation of its DF is quite a difficult problem.

First of all we shall show that in a rarefied electron gas the existence of negative values for a static DF is generally speaking not only possible but inevitable. With this purpose we shall present in somewhat simplified form the arguments contained in the early work by Martin (1967).

Let us consider a quantum one-component plasma in the absence of external charges ($\rho_e=0$). Its DF depends on the value of the parameter $r_S$. As the latter increases, the system gradually changes from the state of an ideal gas to the state of a strongly interacting liquid. At a certain critical value of $r_S^c$ [which is difficult to estimate—see the review by Care and March (1975)] the electron liquid is crystallized and the Wigner crystal appears.[8]

But the appearance of the charge density wave $\delta\rho_i$ with $\mathbf{q}=\mathbf{q}_0$ ($\mathbf{q}_0$ stands for the Wigner crystal period) is only possible provided that the condition

$$\varepsilon(\mathbf{q}_0,0)=0$$

is met. This is a direct consequence of the relation $\varepsilon(\mathbf{q},\omega)\delta\rho_i(\mathbf{q},\omega)=0$ that follows from Eq. (2) at $\rho_e=0$.

[8]It should be noted that another type of phase transition in a one-component plasma with a large $r_S$—a "gas-liquid" transition with a stratification of the system into dense and rarefied phases—has also been discussed in the literature (Kugler, 1975; Wiser and Cohen, 1969; and Van Horn, 1967).

Owing to condition (7), an equilibrium approximation of DF to zero is possible only on the side of negative values. Therefore, even at $r_S < r_S^c$, i.e., in a stable liquid phase, the static DF must be negative.[9] Moreover, as will be shown in Sec. III, it remains negative in a crystal state, too.

To complete the picture, one should also investigate other instabilities which are not connected with charge redistribution. One should make sure that they do not appear until the DF becomes negative and that the redistribution of the system due to these instabilities does not change the sign of the DF.

In the electron system, we speak of the spontaneous appearance of spin density waves. Analysis of the above questions [see Uspenskii (1979); see also Kugler (1975), Kim (1976), and Kimball (1973)] shows that negative values for the DF appear at lower values of $r_S$ than spin density waves. Furthermore, at the transition of the system into a magnetic state, negative values for the DF may be retained. In this connection we should mention the paper by Nagaev (1975) wherein such values were obtained in the investigation of ferromagnetic semiconductors.

## 2. Classical one-component plasma

Going on to the consideration of one-component plasma, we introduce the dynamical structure factor of the system

$$S(\mathbf{q},\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle n_{\mathbf{q}}(t)n_{-\mathbf{q}}(0)\rangle\,, \tag{15}$$

where $n_{\mathbf{q}}(t)$ is a Fourier component of the electron density. The quantity $S(\mathbf{q},\omega)$ determines the Kramers–Kronig relations for the inverse DF [see, for example, Pines and Nozieres (1966)]:

$$\varepsilon^{-1}(\mathbf{q},\omega)=1+\frac{4\pi e^2}{q^2}\int_0^{\infty}\frac{dE^2 S(\mathbf{q},E)}{\omega^2-E^2-i\delta}\,. \tag{16}$$

At a nonzero temperature $T$ the factor $1-\exp(-E/T)$ should be included under the integral sign in Eq. (16).

In the classical limit the temperature $T$ exceeds all the characteristic density oscillation frequencies. This leads to the following expression for the static DF of the classical one-component plasma:

$$\varepsilon^{-1}(\mathbf{q},0)=1-\frac{4\pi n e^2}{Tq^2}S(\mathbf{q})\,, \tag{17}$$

where

$$S(\mathbf{q})=\frac{1}{n}\int_0^{\infty} d\omega\, S(\mathbf{q},\omega) \tag{18}$$

is a static structure factor, and $n$ is the electron density.

In a recent article by Fasolino *et al.* (1978) the static DF of the classical one-component plasma was calculated with the aid of Eq. (17), and estimates of the statistical structure factor (18) were made from the calculations of Hansen (1973) by the method of molecular dynamics. The results are presented in Fig. 1, which illustrates that the static DF is negative in a wide range of values for the parameter $\Gamma=e^2/aT$ $[a=(4\pi n/3)^{-1/3}]$,[10]

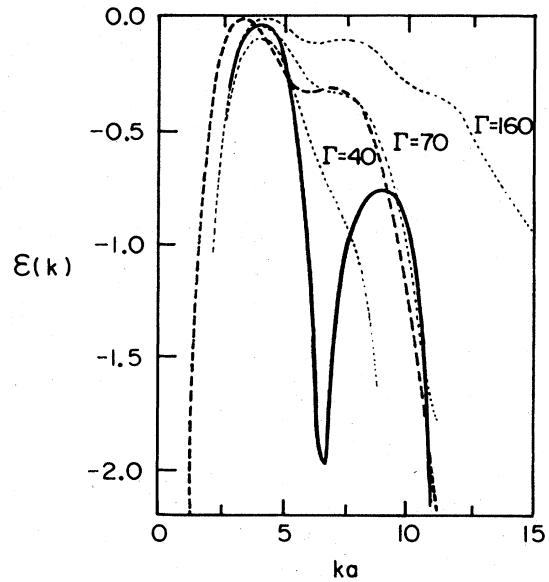


FIG. 1. Statistical dielectric function for classical charged fluids vs wave number. Dotted curves: classical one-component plasma, for three values of plasma parameter $\Gamma$; dashed curve: symmetric molten salt; full curve: molten soldium chloride at 1148 K (Fasolino *et al.*, 1978).

namely, at $40 \lesssim \Gamma \lesssim 160$ for all the values of the momentum $\mathbf{q}$ considered by the authors.

According to calculations by Hansen (1973), at $\Gamma \simeq 170$ in the system under consideration crystallization begins. As can be seen from Fig. 1, at values close to this, the value of the DF at some point $\mathbf{q}_0$ approaches zero, i.e., the boundary of the region of admissible values for the DF (see Sec. I). Therefore, according to what has been said with respect to the quantum plasma, the approach to this boundary leads to the spontaneous appearance of charge density waves with the wave vector $\mathbf{q}_0$, i.e., to a crystallization of the system.

One should bear in mind that as a matter of fact crystallization is a first-order phase transition which proceeds at values of $\Gamma$ less than that at which the curve $\varepsilon(\mathbf{q},0)$ touches the abscissa axis. The latter value characterizes an absolute instability of the system and determines the boundaries of overheating or overcooling for the first-order phase transition.

## 3. Many-component plasma

Concluding this section we shall touch upon the question of the DF of a many-component plasma (a normal electron–ion plasma, liquid metals, melted ion crystals, etc.). Apart from the vast literature devoted to ordinary classical plasma there exist a great many papers studying the DF of a quantum many-component plasma [e.g., Ginoza (1974), March and Tosi (1973), and Tosi, Parrinello, and March (1974)].

The total dielectric function of a many-component plasma can be expressed by formulas (15)–(18), where the quantity $n$ should now be understood as the sum over

[9]This claim was verified in recent calculations by Brosens *et al.* (1980).

[10]In the classical plasma this parameter plays the same role as the parameter $r_S$ in the quantum plasma.

all the plasma components $\sum_i n_i$ (Kimball, 1973).

In Fasolino *et al.* (1978) the data on the static DF are presented for the model of a melted two-component symmetric ion crystal and for molten NaCl. The authors used the results of Hansen and McDonald (1975), who calculated the structure factor by following the methods of molecular dynamics, and (for molten Nacl) the direct neutron measurements of Edwards *et al.* (1975) (see Fig. 1). From this figure it can be seen that in this case the static DF is also negative at all the momenta investigated. Analogous situations will undoubtedly take place for many liquid metals, although as far as we know detailed calculations for these have not as yet been presented.

A model calculation of the DF of liquid metals with account taken of the contribution to polarizability only from heavy ions located in a random field of fast electrons was made by Dallacasa (1977). As can be seen from the expression obtained here for DF [Dallacasa's Eq. (2.22)] this quantity is indeed negative in a wide range of momenta $\mathbf{q}$. Moreover, from the condition $\varepsilon(\mathbf{q},0)=0$ Dallacasa (1977) determines the temperatures of crystallization and the crystal periods appearing for a number of simple metals. These values in his opinion coincide rather well with experimental data.

## III. DIELECTRIC FUNCTION OF CRYSTAL BODIES

### A. Crystal dielectric function matrix

Up to now we have considered only uniform and isotropic media, whose DF depends on the difference between the two coordinates, and the Fourier component on the momentum $\mathbf{q}$ (as well as upon frequency). Owing to the absence of space homogeneity in crystals, the DF becomes a function of both the coordinates separately and, in the momentum representation, of two independent momenta. However, owing to the periodic structure of the crystal, these momenta are not quite arbitrary there, but differ by the reciprocal lattice vector. Accordingly, the DF of a crystal depends on the vectors $\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}'$, where the momentum $\mathbf{q}$ is limited to the first Brillouin zone, and $\mathbf{K}$ and $\mathbf{K}'$ are the reciprocal lattice vectors. Thus the DF of a crystal (and other quantities of the same origin) is a matrix in the vector space $\mathbf{K}$.

#### 1. Definition of the crystal dielectric function

In a homogeneous isotropic system the DF was defined by either of the two equivalent relations (2). The longitudinal DF of a crystal will be defined as a response function which connects the changes of the external $\delta\varphi_e$ and the total $\delta\varphi_t$ electrostatic potential

$$\delta\varphi_e(x)=\int dx'\varepsilon(x,x')\delta\varphi_t(x')\,, \tag{19}$$

where four-dimensional designations $x=(\mathbf{x},t)$ are used. Passing over to the momentum representation ($d^4q=d\mathbf{q}d\omega/(2\pi)^4$)

$$\varepsilon(x,x')=\varepsilon(\mathbf{x},\mathbf{x}',t-t')=\sum_{\mathbf{K}\mathbf{K}'}\int d^4q\,\varepsilon(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}',\omega)\exp[i\omega(t-t')-i(\mathbf{q}+\mathbf{K})\mathbf{x}+i(\mathbf{q}+\mathbf{K}')\mathbf{x}']\,, \tag{20}$$

we obtain

$$\delta\varphi_e(\mathbf{q}+\mathbf{K},\omega)=\sum_{\mathbf{K}'}\varepsilon(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}',\omega)\delta\varphi_t(\mathbf{q}+\mathbf{K}',\omega)\,. \tag{19'}$$

Relations analogous to Eq. (2) are obtained from this one by using the operators $\nabla$ and $\Delta^{-1}$ and take a different form:

$$\delta D_i(\mathbf{q}+\mathbf{K},\omega)=\sum_{\mathbf{K}'}\frac{(\mathbf{q}+\mathbf{K})_i(\mathbf{q}+\mathbf{K}')_j}{|\mathbf{q}+\mathbf{K}'|^2}\varepsilon(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}',\omega)\times\delta E_j(\mathbf{q}+\mathbf{K}',\omega)\,, \tag{21}$$

$$\delta\rho_e(\mathbf{q}+\mathbf{K},\omega)=\sum_{\mathbf{K}'}\frac{|\mathbf{q}+\mathbf{K}|^2}{|\mathbf{q}+\mathbf{K}'|^2}\varepsilon(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}',\omega)\delta\rho_t(\mathbf{q}+\mathbf{K}',\omega)\,. \tag{21'}$$

We shall introduce the inverse matrix $\varepsilon^{-1}(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}',\omega)$ by the relation

$$\sum_{\mathbf{K}'}\varepsilon^{-1}(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}'',\omega)\varepsilon(\mathbf{q}+\mathbf{K}'',\mathbf{q}+\mathbf{K}',\omega)=\delta_{\mathbf{K}\mathbf{K}'}\,.$$

With the aid of this matrix, relations reciprocal to Eqs. (19) and (21) are expressed.

By means of the DF one can express the interaction energy of two external charges $\delta\rho_e^{(1)}(x)$ and $\delta\rho_e^{(2)}(x)$ inside the system. The corresponding correction to the action function

$$\int dx\,\delta\rho_e^{(1)}(x)\delta\varphi_t^{(2)}(x)\,,$$

where $\delta\varphi_t^{(2)}(x)$ is a potential created by the second charge, can be rewritten in the form

$$\int dx\,dx'dx''\delta\rho_e^{(1)}(x)\varepsilon^{-1}(x,x'')V_e(x'',x')\delta\rho_e^{(2)}(x')\,.$$

From this it can be seen that the effective charge interaction "potential" inside the system has the form

$$V_{\text{eff}}(x,x')=\int dx''\varepsilon^{-1}(x,x'')V_c(x'',x')\,,$$

or in the momentum representation

$$V_{\text{eff}}(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}',\omega)=\frac{4\pi}{|\mathbf{q}+\mathbf{K}'|^2}\varepsilon^{-1}(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}',\omega)\,. \tag{22}$$

Here $V_c(x,x')=\delta(t-t')/|\mathbf{x}-\mathbf{x}'|$ is an ordinary Coulomb potential. The matrix (22) must be Hermitian since the correction to the action is real. In the static case when the DF matrix components are real, this gives the following relation important for the future:

$$\varepsilon^{-1}(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}',0)/|\mathbf{q}+\mathbf{K}'|^2=\varepsilon^{-1}(\mathbf{q}+\mathbf{K}',\mathbf{q}+\mathbf{K},0)/|\mathbf{q}+\mathbf{K}|^2\,. \tag{23}$$

#### 2. Macroscopic dielectric function

The matrix character of the DF must be taken into account in our consideration of an effective interaction between particles in the crystal, in lattice dynamics,

and in many other questions. This leads, among other things, to the fact that an action external to the system with a momentum $\mathbf{q}+\mathbf{K}$ evokes a response in all the momenta $\mathbf{q}+\mathbf{K}'$ with an arbitrary inverse lattice momentum $\mathbf{K}'$. This means that even when a system is placed in an external charge field slowly varying in space, with a small momentum $\mathbf{q}$, there appear rapidly oscillating components of the induced charge with vectors $\mathbf{q}+\mathbf{K}$ (or, in other words, with a period of the order of the lattice period).

Nevertheless, for crystals one can also introduce a DF $\varepsilon(\mathbf{q},\omega)$ [Agranovich and Ginzburg (1966); Platzman and Wolff (1973)] which depends on one momentum only and connects the components of the total and external potentials with one and the same momentum,

$$\delta\varphi_e(\mathbf{q},\omega)=\varepsilon(\mathbf{q},\omega)\delta\varphi_t(\mathbf{q},\omega)\,. \tag{24}$$

(Analogous relations connect $\delta\mathbf{D}$ with $\delta\mathbf{E}$ and $\delta\rho_e$ with $\delta\rho_t$.) In fact, let us write Eq. (19′) in the form

$$\delta\varphi_t(\mathbf{q}+\mathbf{K},\omega)=\sum_{\mathbf{K}'}\varepsilon^{-1}(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}',\omega)\delta\varphi_e(\mathbf{q}+\mathbf{K}',\omega)$$

[see Adler (1962), and Wiser (1963)] where on the right-hand side the quantity $\delta\varphi_e$, as distinct from $\delta\varphi_t$, can be chosen arbitrarily (see Sec. II). It could be such that only the component $\delta\varphi_e(\mathbf{q},\omega)$ with $\mathbf{K}=0$ would be nonzero. Then, considering the response of the system, which corresponds to the same momentum $\mathbf{q}$ ($\mathbf{K}'=0$), we have

$$\delta\varphi_t(\mathbf{q},\omega)=\varepsilon^{-1}(\mathbf{q}+0,\mathbf{q}+0,\omega)\delta\varphi_e(\mathbf{q},\omega)\,.$$

From this it is clear that the role of the usual DF in the crystal is played by the quantity

$$\varepsilon(\mathbf{q},\omega)=1/\varepsilon^{-1}(\mathbf{q}+0,\mathbf{q}+0,\omega)\,. \tag{25}$$

At small $|\mathbf{q}|\ll|\mathbf{K}|$ the quantity $\varepsilon(\mathbf{q},\omega)$ is a normal macroscopic DF which determines the connection between electric field and induction, averaged over physically infinitesimal volumes. At high values of $\mathbf{q}$ such an interpretation is impossible. However, in this case the quantity $\varepsilon(\mathbf{q},\omega)$ also keeps its exact microscopic meaning expressed by Eq. (24), although it does not provide complete information about the electrodynamics of the medium contained in the matrix $\varepsilon(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}',\omega)$. We shall call the function $\varepsilon(\mathbf{q},\omega)$ a macroscopic DF of the crystal for arbitrary values of $\mathbf{q}$.

In what follows we are dealing with this function only. In particular, when considering the sign of the DF, which is the key problem here, we shall speak not of a definite sign of the matrix $\varepsilon(\mathbf{q}+\mathbf{K},\mathbf{q}+\mathbf{K}',0)$, but simply of the sign of the macroscopic DF $\varepsilon(\mathbf{q},0)$. It is just to this latter quantity that the general considerations discussed in Sec. II refer, by definition (24).

## 3. Wigner crystal

As a very simple example let us consider a macroscopic DF of a Wigner crystal, i.e., an electron crystal in a system with a homogeneous positive background.

Going back to what has been said in Sec. II.B.2, we ask what will happen to the sign of the static DF for both a quantum and a classical one-component plasma undergoing crystallization. The answer to this question was given as far back as 1964 by de Wette, who suggested that at small $\mathbf{q}$ the static DF of a Wigner crystal must be a negative quantity. A consistent calculation of the DF of a quantum Wigner crystal is a matter of considerable difficulty and has not yet been carried out. In the classical limit the DF of a Wigner crystal was calculated in the work of Bagchi (1969) and has the following form:

$$\frac{1}{\varepsilon(\mathbf{q},\omega)}=1-\frac{\omega_{\mathrm{pl}}^2}{q^2}\sum_\lambda\frac{|\mathbf{q}\mathbf{e}_{\mathbf{q}\lambda}|^2}{\omega^2(\mathbf{q},\lambda)-\omega^2}\,. \tag{26}$$

In this expression

$$\omega_{\mathrm{pl}}^2=\frac{4\pi ne^2}{m}\,,$$

where $m$ is the mass of the particles, $n$ is their density, $\mathbf{e}_{\mathbf{q}\lambda}$ is the phonon polarization vector, and $\omega(\mathbf{q},\lambda)$ is their frequency. As has been established [see Bagchi (1969), and Care and March (1975)], in a cubic Wigner crystal there exist three oscillation branches: two transverse branches with a sound spectrum at small momenta $\mathbf{q}$ and one longitudinal branch with a frequency tending to the plasma frequency $\omega_{\mathrm{pl}}$ at $\mathbf{q}\to 0$. For these frequencies there exists the following sum rule

$$\sum_\lambda\omega^2(\mathbf{q},\lambda)=\omega_{\mathrm{pl}}^2\,. \tag{27}$$

Calculating the maximal value of the right-hand side of Eq. (26) at $\omega=0$ over frequencies $\omega(\mathbf{q},\lambda)$ with account taken of Eq. (27), one can easily see that

$$\frac{1}{\varepsilon(\mathbf{q},0)}\leq 1-\left(\sum_\lambda|\mathbf{n}\mathbf{e}_{\mathbf{q}\lambda}|\right)^2,$$

where $\mathbf{n}=\mathbf{q}/q$. The right-hand side of this inequality is always negative and reaches its maximal (zero) value when the direction of $\mathbf{n}$ coincides with that of one of the polarization vectors $\mathbf{e}_{\mathbf{q}\lambda}$.[11] Hence, the DF of a Wigner crystal is negative for any values of the vector $\mathbf{q}$.

## 4. General dynamic relations

The question of the sign of the DF in a realistic crystal model with two structural components—electrons and ions (nuclei)—will be considered in the next section. Here we shall only present some general relations that describe the crystal as a specific two-component plasma which consists of electrons and oscillating ions. For an effective interaction potential of the electron–ion system [see Eq. (22)] in the harmonic approximation, disregarding the lattice structure, we may use the following expression (Pines, 1963):

$$\frac{V_{\mathbf{q}}}{\varepsilon(\mathbf{q},\omega)}=\frac{V_{\mathbf{q}}}{\varepsilon_{\mathrm{el}}(\mathbf{q},\omega)}+\left(\frac{v_{\mathbf{q}}^i}{\varepsilon_{\mathrm{el}}(\mathbf{q},\omega)}\right)^2\frac{1}{\omega^2-\omega_{\mathbf{q}}^2+i\delta}\,. \tag{28}$$

Here $V_{\mathbf{q}}$ is a Fourier transform of the Coulomb potential, $\varepsilon_{\mathrm{el}}$ is a purely electron DF (rigid lattice), $v_{\mathbf{q}}^i$ is a matrix element of the bare electron–ion interaction,

[11] This follows from the condition $\sum_\lambda(\mathbf{n}\mathbf{e}_{q\lambda})^2=1$ and the inequalities $1\geq|\mathbf{n}\mathbf{e}_{q\lambda}|\geq|\mathbf{n}\mathbf{e}_{q\lambda}|^2$, which become equalities at $\mathbf{n}=\mathbf{e}_{q\lambda}$.

and $\omega_q$ is the phonon frequency. Equation (28) describes the interaction of two charges as the sum of two terms: an interaction in the absence of lattice oscillations and an interaction by means of phonons emitted and absorbed by initial charges due to the renormalized electron–ion interaction $v_q^i/\varepsilon_{el}(q,\omega)$.

When the lattice structure is taken into account and the situation becomes translationally noninvariant, it is more convenient to proceed from the coordinate representation in which the expression for the DF takes the form (Maksimov, 1975; Karakozov and Maksimov, 1978; Dolgov, 1978):

$$\varepsilon^{-1}(x,x')=\varepsilon_{el}^{-1}(x,x')+\sum_{nn'}\int dx_1dx_2dx_3\varepsilon_{el}^{-1}(x,x')\nabla_\alpha v^{ei}(x_1,R_n)D_{nn'}^{\alpha\beta}(t_1-t_2)\nabla_\beta v^{ei}(R_{n'},x_2)\varepsilon_{el}^{-1}(x_2,x_3)V_c^{-1}(x_3,x')\,. \tag{29}$$

Here $\varepsilon_{el}^{-1}$ is an inverse electron DF that takes the periodic potential into account as a rigid nonoscillating lattice, $v^{ei}$ is a pseudopotential of the electron–ion interaction, $n$ is the number of the ion, $R_n$ is its coordinate, $D_{nn'}^{\alpha\beta}$ is the Green's function of ion displacement, $V_c^{-1}$ is an inverse matrix of the Coulomb interaction.

Equation (29) for the inverse DF is of quite a general character and describes any type of crystal (metals, dielectrics, and semiconductors). The specific character of a given crystal is contained in the quantity $\varepsilon_{el}^{-1}$ (an inverse electron DF).

Going on to the momentum representation we shall use Eqs. (20) and

$$D_{nn'}^{\alpha\beta}(t)=\sum_\lambda\int d^4q[\omega^2-\omega_\lambda^2(q)+i\delta]^{-1}\frac{e_\lambda^\alpha(n,q)e_\lambda^\beta(n',q)}{(M_nM_{n'})^{1/2}}\exp[i\omega t-iq(R_n-R_{n'})]\,,$$

where $e_\lambda$ is the phonon polarization vector, $\omega_\lambda(q)$ its frequency, and $M_n$ the ion mass. From this and from Eq. (26) the expression for a static inverse DF determining the macroscopic crystal DF takes the form[12]

$$\begin{aligned}\varepsilon^{-1}(q+0,q+0,0)&=\varepsilon_{el}^{-1}(q+0,q+0,0)\\&-\sum_{\substack{KK'\\ll'}}\frac{e^{i(K'l'-Kl)}}{4\pi e^2(M_lM_{l'})^{1/2}}\frac{|q+K'|^2}{\Omega\omega_\lambda^2(q)}\varepsilon_{el}^{-1}(q+0,q+K,0)v^{ei}(q+K)[q+K,e_\lambda(l',q)]\\&\times[q+K',e_\lambda(l,q)]v^{ei}(q+K')\varepsilon_{el}^{-1}(q+K',q+0,0)\,.\end{aligned} \tag{30}$$

Here we have passed from the summation over $n$ to the summation over the corrdinates of $l$ (with respect to the cell center of the atom inside one cell whose volume is designated by $\Omega$). In addition, we have disregarded the frequency dependence of $\varepsilon_{el}$ in the second item of Eq. (30), since characteristic electron frequencies are much more than phonon frequencies (adiabatic approximations).

Equation (30), where conduction electrons and those entering into the ion composition are considered separately, can be applied to metals. In the general case the potential $v^{ei}(x,R_e)$ should be replaced by the Coulomb potential $Z_le^2/|x-Re|$ ($Z_l$ is the nuclear charge) and at the same time take into account all the electrons of the system. It is convenient to introduce an effective ion charge tensor (Pick *et al.*, 1970)

$$Z_l^{\alpha\beta}(q)=Z_l[\varepsilon_{el}^{-1}(q+0,q+0,0)]^{-1}\times\sum_K\varepsilon_{el}^{-1}(q+0,q+K,0)\frac{q_\alpha(q+K)_\beta}{|q+K|^2}e^{-iKl} \tag{31}$$

which is a microscopic definition of the effective charge introduced by Born in the study of ion crystal dynamics [see Pick (1970)]. Within the limit of small $q$ the quantity (31) vanishes for metals and nonpolar dielectrics; for ion dielectrics the longitudinal part of the tensor $Z_l^{\alpha\beta}$, which indicates screened charge, is transformed in this limit into the ion charge $Z_l$ (Pick *et al.*, 1970).

The entire ion contribution to the macroscopic crystal DF is expressed through the quantity (31), which describes the long-range Coulomb field of an ion. In fact, taking into account Eq. (23), we have

$$\varepsilon^{-1}(q+0,q+0,0)=\varepsilon_{el}^{-1}(q+0,q+0,0)-[\varepsilon_{el}^{-1}(q+0,q+0,0)]^2\sum_{\substack{ll'\lambda\\ \alpha\beta\gamma}}\frac{Z_l^{\alpha\gamma}(q)e_\lambda^\gamma(l,q)Z_l^{\alpha\beta}(q)e_\lambda^\beta(l',q)}{(M_lM_{l'})^{1/2}/\omega_\lambda^2(q)}\,. \tag{32}$$

To conclude this section we should note without giving corresponding general formulas [see Maksimov (1975), Pick *et al.* (1970), Sham (1969), and Keating (1968)] that the phonon frequencies $\omega_\lambda$ themselves depend on the value of the electron DF $\varepsilon_{el}$. This can be seen in the early literature from an elementary formula which refers to the structureless jellium model (Pines, 1963)

$$\omega_q^2=\frac{\omega_{pl}^2}{\varepsilon_{el}(q,0)}\,, \tag{33}$$

where $\omega_{pl}$ is the ion plasma frequency.

### B. Electron and ion parts of the dielectric function

As can be seen from Eqs. (28)–(30), the total inverse crystal DF consists of two parts, one describing polarization properties of electrons in the field of a rigid lattice and the other describing the contribution of the oscillating ions themselves. Now we are in a position to consider these parts separately.

[12]For the sake of simplicity we have considered the pseudopotential to be just a function of the difference of coordinates, although in fact it is a nonlocal operator.

### 1. Electron dielectric function

As has already been noted, the electron DF $\varepsilon_{el}$ corresponds to a rigid lattice whose ion masses are considered infinitely large. In Sec. II we have already emphasized that the DF of a uniform ideal electron gas is positive and that negative values for it could be expected only if exchange and correlation effects were taken into account. The same conclusion is true also for electrons in a periodic lattice field if we take into account the macroscopic DF of the system with infinitely heavy ions. Here we shall concentrate on the role of exchange and correlation effects.

Let us begin with the case of metals whose DF has a singularity at $q \to 0$:

$$\varepsilon_{el}^{-1}(\mathbf{q}+0,\mathbf{q}+0,0) \propto q^2 . \tag{34}$$

In the case of simple metals, which alone will be considered hereafter, nondiagonal matrix elements of the DF are small, since the electron–ion pseudopotential $v^{ei}$ is small (see Sec. I):

$$|\varepsilon_{el}(\mathbf{q}+0,\mathbf{q}+\mathbf{K},0)| \ll \varepsilon_{el}(\mathbf{q}+0,\mathbf{q}+0,0) . \tag{35}$$

Although a number of papers (Wiser, 1963; Moore *et al.*, 1974; Sturm, 1976) are devoted to direct calculation of an electron DF for metals, no reliable results on the sign of this quantity have been obtained by estimating the role of exchange and correlation effects. These effects in real metals (excluding perhaps ferromagnets) are evidently insufficient for their electron DF to become a negative quantity.

Going on to the case of semiconductors and dielectrics [see Gandelman and Ermachenko (1963), Van Vechten and Martin (1972), Onodera (1973), Johnson (1974), Louie *et al.* (1975), Hanke and Sham (1975), Sinha *et al.* (1974), Lannoo (1977), and the review by Hanke (1978)], we should note that at $\mathbf{q} \to 0$ their electron DF tends to a constant limit for which the following designation is used:

$$\lim_{\mathbf{q}\to 0} \varepsilon_{el}^{-1}(\mathbf{q}+0,\mathbf{q}+0,0) \equiv 1/\varepsilon(\infty) .$$

This designation implies that the electron DF coincides with the total one when frequencies exceed phonon frequencies (but are small as compared with characteristic electron frequencies).

One should bear in mind that exchange and correlation effects, which could lead to a negative sign of the electron DF, determine the short-range order in the system and therefore can be considered as manifestations of local field effects in the broad sense of the word. This means that changes in the local structure of the system near a given particle are responsible for the difference between the true field configuration and an averaged one.[13]

In classical macroscopic electrodynamics (e.g., Tamm, 1977) local field effects lead to a difference between the macroscopic DF of the medium and the simple expression

$$\varepsilon = 1 + 4\pi n\alpha$$

and are described by the well known Lorentz–Lorenz formula,

$$\varepsilon = 1 + 4\pi n\alpha/(1-\kappa n\alpha) . \tag{36}$$

Here $\alpha$ is the polarizability of an individual atom, $n$ is the atom density, and $\kappa$ is a numerical constant equal in the simplest cases to $4\pi/3$. From Eq. (36) it can be seen that at high values of polarizability one can hope for the appearance of a negative sign for the DF.

However, it is clear that argumentation based on Eq. (36) cannot be taken seriously, since it refers essentially to the value $\mathbf{q}=0$, for which the DF must be a positive quantity [see Eq. (9)]. In fact, an increase of $\alpha$ may at most cause the DF to diverge with a subsequent reconstruction of the system to a ferroelectric state. This possibility was pointed out long ago by Slater (1967), and the physical causes of the high value of polarizability (particularly in application to the ions $O^{--}$) were discussed by Migoni *et al.* (1976).

Thus, to determine the possibility of a negative DF one must have an expression more general than the Lorentz–Lorenz formula and one which is valid at $\mathbf{q} \neq 0$. Repeated attempts have been made to derive such an expression in the framework of a consistent quantum-mechanical approach (Onodera, 1973; Johnson, 1974; Sinha *et al.*, 1974; Lannoo, 1977). The difficulties encountered by the authors of these papers were overcome by Maksimov and Mazin (1978), who gave a microscopic derivation of the Lorentz–Lorenz formula for dielectrics with strongly bound electrons at $\mathbf{q}=0$. From this paper it can also be seen that at $\mathbf{q} \neq 0$ the formula for the DF is quite different from Eq. (36) and this quantity is not expressed through polarizabilities of individual atoms. In any case, we may state that the values $\varepsilon_{el} < 0$ at $\mathbf{q} \neq 0$ are improbable since the polarization term in the DF decreases rapidly as $q$ increases.

Thus we see that the question of the sign of the electron DF for crystals remains open. There is a suspicion that a negative sign for this quantity would lead to instability of the lattice if the finite ion mass were taken into account, a suspicion which arises when we consider even a simple formula like Eq. (32) leading to $\omega_{\mathbf{q}}^2 < 0$ at $\varepsilon_{el} < 0$. However, this very formula cannot be applied to a real crystal. In particular, for simple metals Uspenskii (1979) has shown the admissibility of negative values for the electron DF, and Kukkonen and Wilkins (1979) have stated that such a situation actually obtains in cesium.

Nevertheless, in what follows we shall proceed from positive values for the electron DF. This assumption only makes stronger our subsequent result for a negative total DF in some classes of solid bodies.

### 2. Ion part of the dielectric function

Let us now turn to the question of whether or not the effects connected with ion oscillations change the sign of the DF and make it negative. As before, we shall begin with metals—only simple ones that have only one atom in the elementary cell.

As has already been emphasized [see Eq. (35)], in simple metals one may disregard nondiagonal components of the matrix $\varepsilon_{el}^{-1}$. This makes it possible to re-

[13]Note that long-range effects (nondiagonal matrix elements of the DF) prevent the emergence of negative DF values (Maksimov and Mazin, 1978).

tain on the right-hand side of Eq. (30) only the terms with $\mathbf{K}=\mathbf{K}'=0$ and simultaneously (in the direction of high symmetry) to discard transversal phonons for which $(\mathbf{q}\mathbf{e}_\lambda)=0$. This leads to a simple expression for the macroscopic DF (Dolgov and Maksimov, 1978):

$$\frac{1}{\varepsilon(\mathbf{q},0)}=\varepsilon_{el}^{-1}(\mathbf{q}+0,\mathbf{q}+0,0)\times\left[1-\frac{\omega_{pl}^2\varepsilon_{el}^{-1}(\mathbf{q}+0,\mathbf{q}+0,0)}{\omega_L^2(\mathbf{q})}\left(\frac{v^{ei}(\mathbf{q})}{V_c(\mathbf{q})}\right)^2\right], \tag{37}$$

where

$$\omega_{pl}=\left(\frac{4\pi NZ^2e^2}{M}\right)^{1/2}$$

is the ion plasma frequency, $\omega_L$ the longitudinal acoustic phonon frequency $v^{ei}$ the electronic–ion interaction pseudopotential, and $V_c=4\pi Ze^2/q^2$ the Coulomb potential.

In the isotropic structureless "jellium" model (Pines and Nozières, 1966; Pines, 1963), where $v^{ei}=V_c$ and $\omega_L^2=\omega_{pl}^2/\varepsilon_{el}$, the electron and ion contributions to the inverse DF completely compensate each other, and, as is well known, the static DF is infinite at all values of $\mathbf{q}$ $[1/\varepsilon(\mathbf{q},0)=0]$. However, in a crystal where apart from longitudinal there also exist transversal oscillation modes, such a balance between electron and ion contributions to the DF can be shifted towards negative values by the quantity $\varepsilon(\mathbf{q},0)$. This is connected with the corresponding decrease of the quantity $\omega_L^2(q)$ due to the existence of sum rules like Eq. (27), which fix the sum $\sum_\lambda\omega_\lambda^2$.

Calculations of $\varepsilon(\mathbf{q},0)$ for simple metals K and Al with the use of real phonon spectra [see, for example, Heine *et al.* (1970)] and for metallic hydrogen using calculational data (Beck and Straus, 1975) were carried out by Dolgov and Maksimov (1978), and the results are presented in Fig. 2. From Fig. 2 it can be seen that the DF of a metal may acquire any value. In Coulomb systems where $V_{ie}(\mathbf{q})=V_c(\mathbf{q})$ (i.e., in metallic hydrogen) the DF is negative at all values of $\mathbf{q}$.

Let us proceed to the case of dielectrics and consider first the limit $\mathbf{q}\to 0$. Rewriting Eq. (32) in this limit so as to apply it to the case of not more than two atoms in

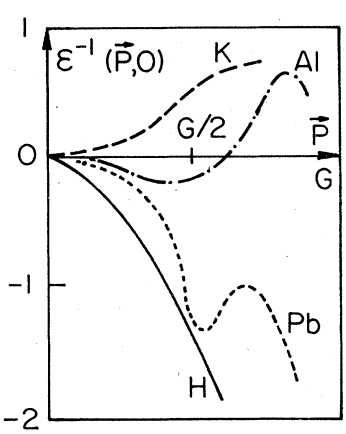


FIG. 2. Static dielectric function for normal metals (K, Al, Pb, and metallic H) vs wave vector in (1, 0, 0) direction (**G**—reciprocal lattice vector).

an elementary cell, we have

$$\frac{1}{\varepsilon(\mathbf{q},0)}=\frac{1}{\varepsilon(\infty)}-\frac{1}{\varepsilon^2(\infty)}\sum_{ll'}\frac{Z_l^{\alpha\gamma}e_L^\gamma Z_l^{\alpha\beta}e_L^\beta}{(M_l M_{l'})^{1/2}\omega_L^2(0)}, \tag{38}$$

where $\varepsilon(\infty)$ is an electron DF (see above). Here we have left only the contribution from the longitudinal optical mode, since other modes make a contribution that vanishes like $q^2$ in the limit $\mathbf{q}\to 0$. In this respect dielectrics differ radically from metals, for which all oscillation modes contribute to the DF at $\mathbf{q}\to 0$. This can be seen from Eq. (32), in which, though the second item vanishes like $q^2$ for all oscillation modes, the first item by virtue of Eq. (34) simultaneously becomes zero according to the same law.

Thus, because of the finite value of the electron DF $\varepsilon(\infty)$ in a dielectric, the relative value of the ion contribution to the total DF decreases considerably. In particular, in nonpolar dielectrics, where such a contribution is altogether absent at $\mathbf{q}\to 0$, the total DF coincides with the electron one:

$$\lim_{\mathbf{q}\to 0}\varepsilon(\mathbf{q},0)=\varepsilon(\infty)\,. \tag{39}$$

Although in polar dielectrics the contribution from the optical mode in Eq. (38) is negative, as in metals, it is always modulo less than $1/\varepsilon(\infty)$. It can be shown (Sinha *et al.*, 1974; Sham, 1969; Dolgov, 1978) that this contribution makes up

$$-\left(1-\frac{\omega_T^2}{\omega_L^2}\right)\Big/\varepsilon(\infty)\,,$$

where $\omega_T$ is the frequency of transverse optical oscillations. This leads to the well know Liddane–Sacks–Teller formula (Cochran and Cowley, 1962):

$$\lim_{\mathbf{q}\to 0}\varepsilon(\mathbf{q},0)=\frac{\omega_L^2}{\omega_T^2}\varepsilon(\infty)\,. \tag{40}$$

The formulas obtained show that at $q\to 0$ the macroscopic DF of a dielectric is a positive quantity. At $q\neq 0$ all oscillation modes contribute to the DF of the dielectric; and since the ion term in Eq. (32) is negative, one may expect, generally speaking, that beginning from some momentum this contribution will exceed the electron contribution and that the total DF in the dielectric will also become negative. Such a situation is most probable in semiconductors with a narrow forbidden band.

It is well known that an electron DF in narrow-band semiconductors (such as Si and Ge) does not differ from a metallic one for sufficiently large wave momenta $|\mathbf{q}|>q_0$, where $q_0\simeq E_g/v_F$. Here $E_g$ is the electron gap in the semiconductor and $v_F$ the Fermi velocity for free electrons with a density equal to that of the valence electrons of the semiconductor. So one may hope that the static macroscopic DF of semiconductors at momenta $|\mathbf{q}|>q_0$ is negative, as in metal. Naturally, to confirm this conclusion one should carry out concrete calculations of the DF in semiconductors.

In concluding this section we shall briefly touch upon the question of the behavior of the DF in the limit $\mathbf{q}\to 0$ and the need for the limiting condition (9), $\varepsilon(\mathbf{q}=0,0)>0$. As we know already, the macroscopic DF in nonconducting crystals (dielectrics and semiconductors) is always positive at $\mathbf{q}=0$. If it appears to be negative at

nonzero values of $\mathbf{q}$, there exists a certain finite momentum $q_0$ determined by the inner system parameters at which the DF may change its sign.

In metals and, in general, in systems with nonlocalized charges the situation is quite different. As shown by Dolgov and Maksimov (1978) and seen from Eq. (37) of the present review, for the simple metals the DF can remain negative up to any arbitrarily low values of $\mathbf{q}$. As follows from the work by Fasolino *et al.* (1978), an analogous situation exists also for one-component and two-component plasmas. Thus in metal there are no inner parameters determining values of the momentum at which the DF becomes positive. In an unbounded metal condition (9) is apparently fulfilled not as the limiting relation $\lim_{q\to 0}\varepsilon(\mathbf{q},0)>0$, but for one singled-out point $\mathbf{q}\equiv 0$.[14] In metals of limited size these characteristic features manifest themselves in momenta $q\sim 1/L$, where $L$ is the crystal dimension, and apparently it is only for such momenta that the macroscopic DF of a metal meets condition (9).

## IV. CONCLUSION

From the considerations presented in the preceding sections it can be seen that the existence of negative values for the static DF contradicts no general principles and moreover that such negative values are possible for a rather wide class of materials. An essential condition here is the absence of a microscopic electroneutrality, as in the case of a Wigner crystal or the presence of nonlocalized charges, as in a metal or molten electrolyte.

In this review we have not considered questions connected with other properties of systems with a negative static DF, excluding the stability property. We have briefly touched upon the relation between high-temperature superconductivity and the sign of the DF (see the appendix). It is clear that these questions require more detailed consideration.

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## APPENDIX: THE SIGN OF THE STATIC DIELECTRIC FUNCTION AND THE PROBLEM OF SUPERCONDUCTIVITY

As we have already mentioned, a very strict restriction on the upper bound for the critical temperature of a superconductor has been derived from the condition $\varepsilon(\mathbf{q},0)>0$ (Cohen and Anderson, 1972; Kirzhnits *et al.*, 1970, 1973). Since this question is very important, we should like to present here the argument of Cohen and Anderson (1972). Then we shall consider this problem taking into account the results obtained in this review.

Cohen and Anderson (1972) proceeded from the known formula for the critical temperature of superconductors,

$$T_c \alpha \omega_0 \exp -\left(\frac{1}{\lambda-\mu^*}\right), \quad \mu^* = \frac{\mu}{1+\mu \ln \varepsilon_F/\omega_0} \tag{A1}$$

which is strictly derived for the case of a weak coupling [see, for example, Kirzhnits *et al.* (1970, 1973)]. Here $\omega_0$ is the characteristic frequency of a phonon, $\varepsilon_F \gg \omega_0$ is the Fermi electron energy, and $\lambda$, $\mu$ are the dimensionless coupling constants of the phonon and Coulomb interactions, respectively. The inhibition of the Coulomb interaction in superconductivity, expressed by the denominator of the formula for $\mu^*$, is a well known effect connected with electron rescattering in a wide (compared to $\omega_0$) region (Bogoliubov *et al.*, 1958).

The quantities $\lambda$ and $\mu$ are directly connected with the effective interaction between electrons by the DF of the system,

$$V_{\text{eff}}(\mathbf{q},\omega) = 4\pi e^2/q^2\varepsilon(\mathbf{q},\omega)\,. \tag{A2}$$

This relation has the form

$$\mu-\lambda = N(0)\langle V_{\text{eff}}(\mathbf{q},0)\rangle\,, \tag{A3}$$

where the brackets imply averaging over the momentum transfer on the Fermi surface, and where $N(0)$ is an electron density of states on this surface. An effective value for the momentum $q$, essential to such an averaging, turns out to be large, i.e., of the order of the Fermi momentum $P_F$.

Equation (A3) shows that if the static DF of the system were positive, the inequality $\lambda \leq \mu$ would hold obligatorily, i.e., the sum of the interactions among electrons would be repulsive. The very appearance of superconductivity, possible only when the inequality $\lambda > \mu^*$ holds, would be due to the above-mentioned effect of the Coulomb interaction inhibition.

From this it immediately follows that the critical temperature has an upper bound. In fact, setting $\lambda=\mu$ in Eq. (A1) (which is the most favorable relation), one can easily see that being a function of $\omega_0$ the quantity $T_c$ has a peak: With the increase of $\omega_0$ it increases at first [due to the increase of the preexponential in Eq. (A1)], then falls (due to the decrease of the logarithm inhibiting Coulomb interaction). The maximum of $T_c$ occurs at $\omega_0=\varepsilon_F e^{-1/\lambda}$ and equals

$$T_c^{\max} = \varepsilon_F e^{-3/\lambda}\,.$$

The value of $T_c^{\max}$ for the small $\lambda$ turns out to be rather low. Taking into consideration some effects of strong coupling, Cohen and Anderson (1972) obtained a rather different formula and they estimated the quantity $T_c^{\max}$ at $\lambda=\mu=\frac{1}{2}$ [15] as a value of the order of 10 K.

It has been mentioned (Kirzhnits, 1977; Maksimov, 1977) that Cohen and Anderson were far from taking into account all the effects which take place in a real metal. Therefore, from the quantitative point of view, this result may be criticized. Moreover, the existence of a negative static DF leads to complete removal of the restrictions on $T_c$ established by Cohen and Anderson (1972).

All preceding considerations in this appendix have been based on Eq. (A2) for the effective interaction among electrons, which holds true only for the weak coupling. To conclude this section we shall briefly touch upon the following question: What effect does the existence of negative values for the DF have upon the

[14]The circumstance that for the DF of a metal the point $q=0$ is singled out has already been emphasized by Izuyama (1973).

[15]At large values of $\mu$ there is a strong tendency to the appearance of ferromagnetism in the system.

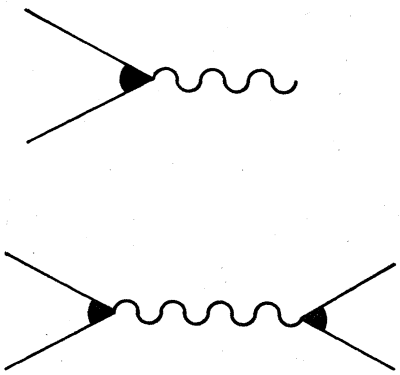

FIG. 3. Effective interaction between two electrons.

effective interaction among electrons?

As we have established already in the case of a one-component plasma, negative values for the DF in this system appear only due to exchange and correlation effects. It is clear that in an effective interaction it is also necessary to take these effects into account. In diagram language this means that we need to introduce the vertex $\Gamma_N$ corrections shown in Fig. 3 by means of triangles. It is clear, nevertheless, that this will not influence the total sign of the effective interaction, since the contribution from vertex parts is described by an essentially positive expression $|\Gamma_N|^2$. At the same time the connection between the sign of the effective electron interaction and the sign of the macroscopic DF of metals is in fact very complicated (particularly in the case of strong coupling) and is far from clear.

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