# Kramers–Kronig relations and the high-frequency expansion for the dielectric constant of systems with Coulomb interaction

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The high-frequency expansion is used to study the validity of the Kramers–Kronig relations (KKR) for the dielectric constant of systems with Coulomb interaction. The KKR are shown to be valid only when the moments are nonnegative. Several criteria for the violation of these relations are derived, and they lead to negative values of the dc dielectric constant. The fact that these criteria are obeyed can be verified on the basis of the experimental data on the structure and thermodynamic properties of real media. It is shown that solution of the problem of violation of the KKR for the dielectric constant is directly related to the type of plasma oscillations in the system.

**1.** Much attention has lately been paid to the theoretical study of the dielectric constant $\varepsilon(q,\omega)$ of CS.[1–9] The reason is that knowing the dielectric constant, we can determine various CS characteristics, such as the themodynamic properties, the structure, the spectrum of collective excitations, and optical properties. Rigorous relations for the dielectric constant play an important role here because they determine the general laws governing the behavior of the dielectric constant as a function of the wave number $q$ and the frequency $\omega$. The first candidate for such relations is the well-known Kramers–Kronig relations (KKR), which for arbitrary CS parameters are valid only for the inverse dielectric constant $\varepsilon^{-1}(q,\omega)$ (Ref. 10). Here the dielectric constants of any material medium for nonzero (but otherwise arbitrary) values of the wave vector $q$ do not necessarily obey the KKR without conflicting with causality and stability requirements.[11] At the same time the problem of the validity of the KKR for the dielectric constant is important for determining the sign of the dc dielectric constant $\varepsilon(q,0)$. When the KKR are valid for $\varepsilon(q,\omega)$, the dc dielectric constant $\varepsilon(q,0)$ is limited in value by the condition[10]

$$\varepsilon(q,0)>1, \tag{1}$$

while the KKR for the inverse dielectric constant $\varepsilon^{-1}(q,\omega)$ allow for negative values of the dc dielectric constant:[10,11]

$$\varepsilon(q,0)<0. \tag{2}$$

At present it is believed that inequality (2) holds because of local field effects, that is, the deviation of the effective field acting on the medium particles from the mean macroscopic field with respect to which the dielectric constant is defined.[12] The inequality (2) is valid only for large local field corrections, which can occur only in highly nonideal systems such as metals and nonideal plasma.[13,14] At the same time, the semiphenomenological methods often used in theoretical investigations of dielectric constants of nonideal CS cannot serve as a sufficient basis for describing the dielectric constants of real media. There are also practically no data on the behavior of the dc dielectric constant $\varepsilon(q,0)$, except for the classical nonideal plasma, whose dielectric constant is determined via Monte Carlo and molecular dynamics methods.[3]

One must accept the results of numerical studies of classical CS cautiously, however. The point is that at present there exists a rigorous proof of stability of electroneutral CS only when the negatively and/or positively charged particles are fermions[15] (see also Ref. 16). There is one more essential factor directly related to the stability of CS and involving the most extensively studied model of a one-component plasma (OCP). According to the results of numerical studies, both the classical[17] and the degenerate quantum[18] ocp have a negative isothermal compressibility $\varkappa_T$ for fairly high values of the nonideality parameter, which contradicts the well-known thermodynamic stability condition[19]

$$\varkappa_T>0. \tag{3}$$

Although attempts have been made[3,6] to explain the violation of condition (3) in OCP, the problem cannot yet be considered resolved. More than that, with allowance for the exact limiting relation for the dc dielectric constant $\varepsilon(q,0)$ of OCP,[10]

$$\lim_{q\to 0} q^2(\varepsilon(q,0)-1)=4\pi z_a{}^2e^2n_a{}^2\varkappa_T, \tag{4}$$

where $n_a$ is the mean number density of particles with charge $z_a e$ and mass $m_a$, the problem of violating condition (3) is directly related to the problem of negative values of the dielectric constant $\varepsilon(q,0)$ in ocp. In any case, the existing numerical calculation data lead to negative values of the dc dielectric constant precisely for values of ocp thermodynamic parameters with $\varkappa_T<0$ (see Refs. 3 and 6).

This attaches great importance to the problem of confirming that the dc dielectric constant can be negative [or the violation of KKR for $\varepsilon(q,\omega)$] of real media, where the thermodynamic stability condition (3) is sure to be met. In view of what has been said about solution of this problem, there is need for such additional information on the behavior of the dielectric constant as the high-frequency expansion in powers of $1/\omega^2$, which is determined by the dielectric-constant moments. In this connection Ref. 20 should be mentioned. There modified KKR for the dielectric constant were derived and the relation between the characteristics of the additional pole term and the high-frequency expansion for the dielectric constant was discussed.

In this paper the high-frequency expansion is used to directly analyze the KKR for the dielectric constant. These relations are shown to be valid only for nonnegative values of the moments. The exact expression for the second moment is used to derive a number of criteria for violation of the KKR for the dielectric constant. These in turn lead to negative values of the dc dielectric constant. On the basis of this it is found that the CS in which the plasma oscillation spectrum $\Omega(q)$ lies below the plasma frequency $\omega_p$ have a negative dc dielectric constant.

**2.** Further discussion will be done on the assumption that the KKR for the dielectric constant hold true:

$$\operatorname{Re}\varepsilon(q,\omega)-1=-\frac{1}{\pi}P\int_0^\infty \frac{d\alpha^2}{\omega^2-\alpha^2}\operatorname{Im}\varepsilon(q,\alpha), \tag{5}$$

$$\operatorname{Im}\varepsilon(q,\omega)=\frac{2\omega}{\pi}P\int_0^\infty \frac{d\alpha}{\omega^2-\alpha^2}(\operatorname{Re}\varepsilon(q,\alpha)-1). \tag{6}$$

Allowing for the fact that the imaginary part of the dielectric constant is nonnegative for $\omega\geqslant 0$ (see Ref. 10),

$$\operatorname{Im}\varepsilon(q,\omega)\geqslant 0 \tag{7}$$

we see that Eq. (5) directly implies inequality (1), which is the necessary and sufficient condition for the validity of the KKR for the dielectric constant.[11] At the same time, according to (5), the real part of the dielectric constant, $\operatorname{Re}\varepsilon(q,\omega)$, can be represented in the high-frequency limit as an expansion in powers of $1/\omega^2$:

$$\operatorname{Re}\varepsilon(q,\omega)\underset{\omega\to\infty}{=}1-\sum_{n=1}^{\infty}\frac{m_n(q)}{\omega^{2n}}, \tag{8}$$

where the dielectric-constant moments $m_n(q)$ are defined as

$$m_n(q)=\frac{1}{\pi}\int_0^\infty d\alpha^2\alpha^{2n-2}\operatorname{Im}\varepsilon(q,\alpha). \tag{9}$$

Combining Eq. (9) with Eq. (7), we find that for the KKR for the dielectric constant to be valid the moments $m_n(q)$ must be nonnegative:

$$m_n(q)\geqslant 0. \tag{10}$$

Thus, violation of inequality (10) for any moment $m_n(q)$ indicates that the KKR for the dielectric constant have broken down. One must bear in mind that satisfying condition (10) for a finite number of moments does not guarantee that these relations are valid for a given value of the wave vector $q$. More than that, it is possible in principle that inequality (10) is violated for a certain moment $m_n(q)$ only within a definite range of wave vectors.

To determine the moments $m_n(q)$ we employ the high-frequency expansion for the real part of the inverse dielectric constant:

$$\operatorname{Re}\varepsilon^{-1}(q,\omega)\underset{\omega\to\infty}{=}1+\sum_{n=1}^{\infty}\frac{M_n(q)}{\omega^{2n}}, \tag{11}$$

$$M_n(q)=-\frac{1}{\pi}\int_0^\infty d\alpha^2\alpha^{2n-2}\operatorname{Im}\varepsilon^{-1}(q,\alpha), \tag{12}$$

where, with allowance for (7), the moments $M_n(q)$ of the inverse dielectric constant must be nonnegative,

$$M_n(q)\geqslant 0, \tag{13}$$

for all wave vectors for arbitrary thermodynamic CS parameters, since Eqs. (11) and (12) are corollaries of the KKR for $\varepsilon^{-1}(q,\omega)$, which are always valid.[10] Bearing in mind that in the high-frequency limit the imaginary part of the dielectric constant is smaller than any finite power of $\omega$ (Ref. 21),

$$\lim_{\omega\to\infty}\omega^{2n}\operatorname{Im}\varepsilon(q,\omega)=0, \tag{14}$$

and combining this with (8) and (11), we obtain

$$\operatorname{Re}\varepsilon(q,\omega)\underset{\omega\to\infty}{=}1+\sum_{k=1}^{\infty}\sum_{n=1}^{\infty}\sum_{l=1}^{k}\frac{(-1)^k k!}{(k-l)!\,l!}\frac{M_n{}^l(q)}{\omega^{2nl}}. \tag{15}$$

For one thing,

$$m_1(q)=M_1(q),\quad m_2(q)=M_2(q)-M_1^2(q). \tag{16}$$

Hence, under condition (13) the inequality (10) is always true for $m_1(g)$, while it may be violated from $m_2(q)$ if

$$M_2(q)<M_1^2(q). \tag{17}$$

Thus,

$$m_2(q)<0 \tag{18}$$

can be considered a sufficient condition for violation of the KKR for the dielectric constant. Hence, in the range of wave vectors and CS thermodynamic parameters where the inequalities (17) and (18) are valid the dc dielectric constant is negative. Note that the inverse statement is generally not true.

**3.** A realistic estimate of the validity of (17) and (18) is possible only if we know the specific expressions for $M_1(q)$ and $M_2(q)$, which can easily be obtained (the corresponding calculations are detailed in Refs. 22 and 23) if one allows for the relation between the inverse dielectric constant and the charge-charge response function.[10] As a result we get

$$M_1(q)=m_1(q)=\omega_p^2, \tag{19}$$

$$M_2(q)=m_2(q)+\omega_p^4, \tag{20}$$

$$m_2(q)=\sum_a\omega_a^2\left(\frac{2\langle\hat{T}_a\rangle q^2}{m_a}+\frac{\hbar^2q^4}{4m_a^2}\right)$$
$$+\sum_{ab}(n_an_b)^{1/2}\int_0^\infty dk k^2(S_{ab}(k)-\delta_{a,b})\left\{\frac{z_a^2z_b^2e^4}{m_am_b}\right.$$
$$\left.\times\left(\frac{(q^2-k^2)}{kq^3}\ln\left|\frac{q+k}{q-k}\right|-\frac{2k^2}{q^2}+6\right)-\frac{8z_a^3z_be^4}{3m_a^2}\right\}. \tag{21}$$

Here

$$\omega_a=(4\pi z_a^2e^2n_a/m_a)^{1/2}$$

is the plasma frequency for particles of species $a$,

$$\omega_p=\left(\sum_a\omega_a^2\right)^{1/2},$$

$S_{ab}(q)$ is the static structure factor for particles of species $a$ and $b$ and is related directly to the respective correlation function $g_{ab}(r)$ (see Ref. 10),

$$S_{ab}(q)=\delta_{a,b}+(n_an_b)^{1/2}\int dr\exp(iqr)(g_{ab}(r)-1), \tag{22}$$

and $\langle\hat{T}_a\rangle$ is the exact mean kinetic energy per particle of $a$

species, which in the classical limit ($\hbar \to 0$) is

$$\langle \hat{T}_a \rangle = {}^3/_2 T. \tag{23}$$

In deriving Eq. (21) we used the Coulomb interparticle interaction potentials,

$$u_{ab}(q) = 4\pi z_a z_b e^2/q^2. \tag{24}$$

According to Eq. (21), the second dielectric-constant moment $m_2(q)$ is fully determined by the mean kinetic energy and the static structure factors $S_{ab}(q)$. The factors can be measured directly in experiments in which particle beams and photons are scattered.[24] As for the mean kinetic energy $\langle \hat{T}_a \rangle$, fairly rigorous estimates can be obtained. As it happens, in many cases heavy charged particles in real disordered CS can be treated by classical statistics with the use of (23). The mean kinetic energy of electrons can easily be determined on the basis of the experimental values of pressure $P$, which in a CS, according to the virial theorem,[19] is

$$P = {}^2/_3 \sum_a n_a \langle \hat{T}_a \rangle + {}^1/_3 \langle \hat{U} \rangle. \tag{25}$$

The mean potential energy per unit volume, $\langle \hat{U} \rangle$, can also be calculated using the experimentally measured structure factors $S_{ab}(q)$:

$$\langle \hat{U} \rangle = \sum_{ab} \langle \hat{U}_{ab} \rangle, \tag{26}$$

$$\langle \hat{U}_{ab} \rangle = {}^1/_2 (n_a n_b)^{1/2} \int \frac{d^3q}{(2\pi)^3} u_{ab}(q) \, (S_{ab}(q) - \delta_{a,b}).$$

Thus, condition (18) for violation of the KKR for the dielectric constant can be verified fairly rigorously for real CS by employing the experimental data on the structure and the equation of state.

Several useful results follow directly from Eq. (21) when analyzing the behavior of $m_2(q)$ in the long-wave limit of $q \to 0$. Indeed,

$$m_2{}^0 = \lim_{q\to 0} m_2(q)$$
$$= \frac{8}{3} \sum_{a\neq b} (n_a n_b)^{1/2} \left\{ \frac{z_a^2 z_b^2 e^4}{m_a m_b} - \frac{z_a^3 z_b e^4}{m_a^2} \right\} \int_0^\infty dk k^2 S_{ab}(k). \tag{27}$$

Combining Eq. (27), definition (22), the fact that

$$S_{ab}(k) = S_{ba}(k), \tag{28}$$

and the electroneutrality condition, for a two-component electron-ion CS we get

$$m_2{}^0 = \frac{\omega_e{}^4}{3} \left( 1 + \frac{z_i m_e}{m_i} \right)^2 (g_{ei}(0) - 1). \tag{29}$$

Thus, if

$$0 < g_{ei}(0) < 1 \tag{30}$$

holds in a two-components CS, the KKR for the dielectric constant of such a system are invalid in the limit of $q \to 0$ and hence

$$\varepsilon(q \to 0, 0) < 0. \tag{31}$$

Note that formula (29) for $m_0^2$ is valid only for the Coulomb interparticle interaction potentials (24) and, therefore, is invalid for two-component classical plasma unstable against the Coulomb electron-ion interaction.[21] For such a system,

$$m_2{}^0 = -\frac{\omega_e{}^2 z_i{}^{1/2}}{3m_e} \left( 1 + \frac{z_i m_e}{m_i} \right)^2 \int \frac{d^3k}{(2\pi)^3} k^2 u_{ei}(k) S_{ei}(k). \tag{32}$$

Here the potential $u_{ei}(k)$ is defined by (24) only in the limit of $k \to 0$. As Eq. (32) implies, the possibility of $m_2^0$ assuming negative values stems from the fact that $S_{ei}(k)$, in contrast to $S_{aa}(k) > 0$, has no fixed sign.

For an ocp, Eqs. (27)–(29) imply

$$m_2{}^0 = 0, \tag{33}$$

which confirms the validity of the limiting relation for arbitrary thermodynamic parameters[25] [see Eqs. (8) and (19)]:

$$\varepsilon(q \to 0, \omega) = 1 - \omega_p{}^2/\omega^2. \tag{34}$$

In this connection we must examine the size of $m_2(q)$ to within $q^2$. Equation (21) implies

$$m_2(q) \approx m_2{}^0 + \left\{ \sum_a \frac{2\omega_a{}^2 \langle \hat{T}_a \rangle}{m_a} + \sum_{ab} \frac{16\pi z_a z_b e^2}{15 m_a m_b} \langle \hat{U}_{ab} \rangle \right\} q^2. \tag{35}$$

Thus, if we allow for (18), we conclude that the KKR for the dielectric constant of an ocp of particles of species $a$ with the compensating background are violated in the range of small wave vectors $q$ provided that

$$-2\langle \hat{U}_{aa} \rangle / 15 n_a \langle \hat{T}_a \rangle > 1. \tag{36}$$

This forces the dc dielectric constant of an ocp to become negative in the case of strong collisionality and a negative mean potential energy. One must bear in mind here that according to Eq. (25) the pressure in ocp is already negative for

$$-\langle \hat{U}_{aa} \rangle / 2 n_a \langle \hat{T}_a \rangle > 1. \tag{37}$$

If the problem of thermodynamic stability of ocp is ignored, inequality (36) combined with the limiting relation (4) agree with (37) and the data of computer calculations for classical ocp.[2,3,6]

**4.** These problems are directly linked to the studies of the spectrum $\Omega(q)$ of plasma oscillations in CS. This aspect has lately attracted great attention in the literature owing to the fact that in highly collisional CS the $\Omega(q)$ spectrum may lie below the plasma frequency $\omega_p$:

$$\Omega(q) < \omega_p, \tag{38}$$

in contrast to weakly collisional CS.[2,3,6,26,27]

A theoretical study of the spectrum of plasma oscillations, $\Omega(q)$, is based on an examination of the dispersion equation[10]

$$\varepsilon(q, z) = 0, \tag{39}$$

which is solved for a fixed value of the wave vector $q$ at complex-valued frequencies $z$ with $\text{Im}\, z < 0$. For well-defined oscillation,[5]

$$\left| \frac{\text{Im}\, z(q)}{\text{Re}\, z(q)} \right| \ll 1, \tag{40}$$

the only oscillations of interest, the spectrum $\Omega(q) = \text{Re}\, z(q)$ is a solution of the equation

$$\text{Re}\,\varepsilon(q,\omega)=0. \quad (41)$$

Here

$$\text{Im}\, z(q) = -\left\{\frac{\partial\, \text{Re}\,\varepsilon(q,\omega)}{\partial\omega}\right\}^{-1} \text{Im}\,\varepsilon(q,\omega)\,|_{\omega=\Omega(q)}. \quad (42)$$

Condition (40) leads to the appearance of well-defined peaks in the dynamic structure factor[10]

$$S(q,\omega) = \frac{\hbar q^2}{2\pi(1-\exp(-\hbar\omega/T))} \frac{\text{Im}\,\varepsilon(q,\omega)}{|\varepsilon(q,\omega)|^2} \quad (43)$$

at a fixed value of the wave vector $q$ in the neighborhood of the frequencies $\omega = \Omega(q)$ specified by Eq. (41). This fact is used to extract information about the spectrum $\Omega(q)$ in experiments in inelastic scattering of electron beams.[28] Such information exists at present for a fairly broad class of disordered CS, including the classical nonideal plasma.[26,27]

The reader will note that according to (8) and (21) the high-frequency expansion of the real part of the dielectric constant of a weakly nonideal CS is

$$\text{Re}\,\varepsilon(q,\omega) \approx 1 - \frac{\omega_p^2}{\omega^2} - \frac{m_2^{\text{ideal}}(q)}{\omega^4}, \quad (44)$$

where the moment $m_2^{\text{ideal}}$ leaves out the integrated Coulomb interaction:

$$m_2^{\text{ideal}}(q) = \sum_a \omega_a^2 \left( \frac{2\langle \hat{T}_a\rangle^{\text{ideal}} q^2}{m_a} + \frac{\hbar^2 q^4}{4m_a^2} \right). \quad (45)$$

But formulas (44) and (45), as is known,[21] serve to determine the spectrum $\Omega(q)$ of plasma oscillations in a weakly nonideal CS in the range of small wave vectors. This means that in such systems the high-frequency expansion (8) has a radius of convergence in frequency that includes the near-plasma-frequency range, $\omega \sim \omega_p$. Here Eqs. (41), (44), and (45) imply

$$\Omega(q) > \omega_p. \quad (46)$$

Hence, inequality (38) is valid only for strongly nonideal CS.

Allowing for the above argument, we can assume that the radius of convergence of the high-frequency expansion (8) for the dielectric constant encompasses the near-plasma-frequency range for arbitrary thermodynamic parameters at least in the region of small wave vectors. Then, by analogy with the case of a weakly nonideal CS, the dispersion equation for determining the spectrum $\Omega(q)$ of plasma oscillations can be written as

$$\text{Re}\,\varepsilon(q,\omega) \approx 1 - \frac{\omega_p^2}{\omega^2} - \frac{m_2(q)}{\omega^4} = 0, \quad (47)$$

which is corroborated by the results of applying models of the dielectric constant of a classical ocp that are based on the use of moments and are in good agreement with the results of computer simulations.[3,9] But from (47) it follows that inequality (38) is valid only if condition (18) is met.

Thus, if the spectrum of plasma oscillations, $\Omega(q)$, for certain values of $q$ lies below the plasma frequency $\omega_p$, for certain wave vectors the KKR for the dielectric constant become invalid and the dc dielectric constant negative. The inverse statement is generally untrue.

This offers the possibility of verifying experimentally the existence of real disordered CS with a negative dc dielectric constant.


[1]S. Ichimaru, H. Totsyji, T. Tange, and D. Pines, Prog. Theor. Phys. **54**, 1077 (1975).
[2]G. Kalman and P. Carini (eds.), *Strongly Coupled Plasmas*, Plenum Press, New York (1978).
[3]M. Baus and J. P. Hansen, Phys. Rep. **59**, 1 (1980).
[4]V. D. Gorobchenko and E. G. Maksimov, Usp. Fiz. Nauk **130**, 65 (1980) [Sov. Phys. Usp. **23**, 35 (1980)].
[5]P. Carini, G. Kalman, and K. J. Golden, Phys. Lett. **78A**, 450 (1980).
[6]S. Ichimaru, Rev. Mod. Phys. **54**, 1017 (1982).
[7]R. Cauble and D. B. Boercker, Phys. Rev. A **28**, 944 (1983).
[8]S. Ichimaru, H. Iyetomi, and S. Tanaka, Phys. Rep. **149**, 93 (1987).
[9]S. V. Adamjan, T. Meyer, and I. M. Tkachenko, Contrib. Plasma Phys. **29**, 373 (1989).
[10]D. Pines and Ph. Nozière, *The Theory of Quantum Liquids*, Benjamin, New York (1966).
[11]D. A. Kirzhnits, Usp. Fiz. Nauk **119**, 367 (1976).
[12]O. V. Dolgov and E. G. Maksimov, Usp. Fiz. Nauk **135**, 441 (1981).
[13]O. V. Dolgov and E. G. Maksimov, Pis'ma Zh. Eksp. Teor. Fiz. **28**, 3 (1978) [JETP Lett. **28**, 1 (1978)].
[14]A. Fasolino, M. Parrinello, and M. P. Tosi, Phys. Lett. **66A**, 119 (1978).
[15]F. J. Dyson and A. Lenard, J. Math. Phys. **8**, 423 (1967).
[16]J. Lebowitz and E. Lieb, Phys. Rev. Lett. **22**, 631 (1969).
[17]W. L. Slattery, G. D. Doolen, and H. E. De Witt, Phys. Rev. A **26**, 2255 (1982).
[18]D. M. Ceperley and B. J. Adler, Phys. Rev. Lett. **45**, 566 (1980).
[19]L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Part 1, 3rd ed., Pergamon Press, Oxford (1980).
[20]V. V. Losyakov, Kratk. Soobshch. Fiz., No. 5, 35 (1983).
[21]W.-D. Kraefty, D. Kremp, W. Ebeling, and G. Röpke, *Quantum Statistics of Charged Particle Systems*, Akademie-Verlag, Berlin (1986).
[22]S. V. Adamyan, T. Meyer, and I. M. Tkachenko, Fiz. Plasmy **11**, 826 (1985) [Sov. J. Plasma Phys. **11**, 481 (1985)].
[23]T. Meyer and I. M. Tkachenko, Contrib. Plasma Phys. **25**, 437 (1985).
[24]D. Pines, *Elementary Excitations in Solids*, Benjamin, New York (1963).
[25]J. P. Hansen and I. R. McDonald, Phys. Rev. Lett. **41**, 1379 (1978); Phys. Rev. A **23**, 2041 (1981).
[26]N. March and M. Parrinello, *Collective Effects in Solids and Liquids*, Adam Hilger, Bristol (1982).
[27]V. B. Bobrov, V. D. Ozrin, and S. A. Trigger, Physica A **164**, 453 (1990).
[28]J. P. Hansen, I. R. McDonald, and E. L. Pollock, Phys. Rev. Lett. **32**, 277 (1974); Phys. Rev. A **11**, 2111 (1975).


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