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The charge structure function in electrolytes and polyelectrolytes

G. Jannink [a] and J.R.C. van der Maarel [b]

[a] *Laboratoire Léon Brillouin (CEA-CNRS), CEN-Saclay, 91191 Gif-sur-Yvette cedex (France)*
[b] *Department of Physical and Macromolecular Chemistry, Gorlaeus Laboratories, University of Leiden, P.O. Box 9502, 2300 Leiden (Netherlands)*

Abstract

The relation between charge and dielectric structure functions is examined in the case of electrolytes and polyelectrolytes. When the coupling constant is larger than unity, characteristic features should be observed on the dielectric structure function, in addition to the classical screening effect. We point our the existence of experimental conditions which provide direct information of the dielectric structure at shorter wavelength ($\lambda \leqslant 1$ nm). They correspond to zero average contrast in scattering experiments.

Keywords: Charge structure function; Polyelectrolytes; Electrolytes; Dielectric structure function

1. Introduction

Charged systems possess chemical and electric susceptibilities: they respond in a characteristic manner to concentration and charge gradients. The two susceptibilities are naturally linked and several authors [1,2] have studied their relation for instance in electrolytes, molten salts and plasmas. One of the main results of this approach is to provide the structure of the charges associated with the screening of the Coulomb interaction, in the limit of zero reciprocal space vector, q^{-1}. Also the screening length is generally [3] found to increase with q, which makes strong fluctuation in the charge structure possible at shorter wavelength.

In the case of polyelectrolytes this point of view has not yet been developed. There exists a large body of evidences [4] for dielectric properties. On the other hand, the partial structure functions are being studied [5–7] both theoretically and experimentally. It is therefore of interest to determine the contribution of the charge structure function to the electric response especially because the Coulomb coupling constant associated with the polyion has a value greater than unity.

There are nevertheless several difficulties. Dielectric phenomena in polyelectrolytes are very complex. Also, we do not know what the equilibrium conformation of the polyion is at a given concentration: this conformation is related in a self consistent manner to the screening of the Coulomb interaction. A similar obstacle is found in simple electrolytes if one accounts for the electronic cloud deformation around the ions.

There are however reasons to be confident in this approach. A simple relation exists for instance between the accumulation of charges around the polyion-water interface, and oscillation [7] of the partial (+, −) structure function: such oscilla-

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tions should be found in the dielectric structure function. On the other hand, there exists an interesting experimental situation. Namely, applying the zero average contrast [8] method to the polyion counterion system, we can measure directly the charge structure function and, consequently, the ionic dielectric susceptibility.

In what follows, we discuss the relations which are useful in this investigation. We consider a simple model to illustrate the case and we point out the unsolved problem.

2. The charge structure function in polyelectrolytes: two possible definitions

The charge structure function related to the charge fluctuation

$$\sum_{A=1}^{2} Z_A C_A(r)$$

where $C_A(r)$ is the local concentration of molecule of type A and Z_A its charge (for instance $A=1$ refers to the polyion and $A=2$ refers to the counterion). Overall electrical neutrality requires $|Z_1C_1| = |Z_2C_2|$ which we shall further denote by ZC. We consider:

$$\begin{aligned} Z^2C^2H_{ZZ}(q) &= \int \mathrm{d}^3r\, \mathrm{e}^{\mathrm{i}q\cdot r} \left\langle \left\{ \sum_{A=1}^{2} Z_A C_A(r) \right\} \left\{ \sum_{B=1}^{2} Z_B C_B(0) \right\} \right\rangle \\ &= \sum_{A=1}^{2} \sum_{B=1}^{2} Z_A Z_B C_A C_B H_{AB}(q) \qquad (1) \end{aligned}$$

where

$$H_{AB}(q) = \int \mathrm{d}^3r\, \mathrm{e}^{\mathrm{i}q\cdot r} \left\{ \frac{\langle C_A(r) C_B(0) \rangle}{C_A C_B} - 1 \right\} \qquad (2)$$

are the partial structure function.

By definition, this function decomposes in two parts

$$H_{AB}(q) = \delta_{AB} \frac{h_A(q)}{C_A} + H_{AB}^{II}(q) \qquad (3)$$

where $h_A(q)$ is the normalized form function and where $H_{AB}^{II}(q)$ is the *distinct* partial structure.

2.1 Rigid spherical molecules

In the case of rigid spherical molecules it is convenient to introduce the partial structure *factor* [7]

$$\begin{aligned} S_{AB}(q) &= \sqrt{C_A C_B}\, H_{AB}(q) / \sqrt{h_A(q) h_B(q)} \\ &= \delta_{AB} + \sqrt{C_A C_B}\, H_{AB}^{II} / \sqrt{h_A(q) h_B(q)} \qquad (4) \end{aligned}$$

These factors do not depend any more on the form function of the molecules. We can write

$$\begin{aligned} ZCH_{ZZ}(q) &= \sum_{A=1}^{2} \sum_{B=1}^{2} (-1)^A (-1)^B \\ &\quad \times \sqrt{Z_A Z_B}\, S_{AB}(q) \sqrt{h_A(q) h_B(q)} \qquad (5) \end{aligned}$$

and we define

$$S_{ZZ}(q) = \sum_{A=1}^{2} \sum_{B=1}^{2} (-1)^A (-1)^B \sqrt{Z_A Z_B}\, S_{AB}(q) \qquad (6)$$

as the molecular charge structure factor.

2.2 Flexible polyions

In the case of flexible polyions, it is appropriate ot introduce the concentration C_A in charge carriers. If each monomer carries a charge, C_A is the monomer concentration. We assume also that each counterion bears a single charge. Let $f_A(q)$ be the monomer form function. In analogy with eq. (4), we define

$$S_{AB}(q) = \sqrt{C_A C_B}\, H_{AB}(q) / \sqrt{f_A(q) f_B(q)} \qquad (7)$$

We are however interested in the reciprocal space interval $q \cdot a < 1$, where a is the size of a monomer. In such an interval, $f_A(q) \simeq 1$ and

$$S_{AB}(q) = \sqrt{C_A C_B}\, H_{AB}(q) \qquad (8)$$

is the partial structure factor.

Overall neutrality requires

$$C_A = C_B = C$$

and therefore

$$CH_{ZZ}(q) = S_{ZZ}(q) = \sum_{A=1}^{2} \sum_{B=1}^{2} (-1)^A (-1)^B S_{AB}(q) \qquad (9)$$

This defines the charge structure factor for flexible, linear polyelectrolytes. Effects due to the polyion form function are now included in this definition.

In general, the structure of a two component systems such as a polyelectrolyte is described by type set $\{S_{AB}(q)\}$ of partial structure factors. However, as pointed out by March and Tosi [1], we may as well use combinations of such factors. These are the compound structure factors, i.e. the charge structure factor (9), the number structure factor

$$S_{NN}(q) = \sum_{A=1}^{2} \sum_{B=1}^{2} S_{AB}(q) \qquad (10)$$

and the cross correlation term

$$S_{NZ}(q) = S_{AA}(q) - S_{BB}(q) \qquad (11)$$

The two sets of factors are equivalent.

In the case of electrically charged molecules, the set of compound structure factors is more appropriate because it can be related to the electric susceptibility. For instance, sum rules can be derived (see next section).

We wish to emphasize that the charge structure function can be determined directly from a single scattering experiment. Consider namely the general expression for the scattered intensity

$$I = \sum_{A,B=1}^{2} b_A b_B C_A C_B H_{AB}(q) \qquad (12)$$

where b_1, b_2 are respectively the contrast length of the polyion monomer and counterion. Zero average contrast is defined by the situation $b_1 = -b_2 = b$. In this case

$$I = b^2 C^2 H_{ZZ}(q) = b^2 C S_{ZZ}(q) \qquad (13)$$

which si the relation searched for.

3. Dielectric and charge structure functions

A general outline of the dielectric response theory is found in reference [9]. We are concerned with the dielectric structure at zero frequency. For this, we consider the response $E(q, \omega)$ to an applied longitudinal field $D(q, \omega)$

$$E(q, \omega) = \frac{1}{\epsilon(q, \omega)} D(q, \omega) \qquad (14)$$

Let $\delta C_e(q, \omega)$ be an (infinitesimal) external negative charge density, and $\delta C_Z(q, \omega)$ the associated polarization of internal charges. We define

$$\delta C_Z(q, \omega) = \sum_{A=1}^{2} Z_A \delta C_A(q, \omega) = \delta C_-(q, \omega) - \delta C_+(q, \omega) \qquad (15)$$

With help of Maxwell's equation, we write

$$\frac{1}{\epsilon(q, \omega)} = 1 + \frac{\delta C_Z(q, \omega)}{\delta C_e(q, \omega)} \qquad (16)$$

On the other hand, the "atomic" response $\chi_{ZZ}(q, \omega)$ to a perturbation $U(q, \omega)$ is by definition

$$\delta C_Z(q, \omega) = -\chi_{ZZ}(q, \omega) U(q, \omega) \qquad (17)$$

with the Poisson equation, the perturbation $U(q, \omega)$ can be written in the form

$$U(q, \omega) = -V(q) \delta C_e(q, \omega) \qquad (18)$$

where

$$V(q) = \frac{4\pi e^2}{\epsilon_0 q^2} \qquad (19)$$

Combining eqs. (16), (17) and (18) we find

$$\frac{1}{\epsilon(q, \omega)} = 1 + \frac{4\pi e^2}{\epsilon_0 q^2} \chi_{ZZ}(q, \omega) \qquad (20)$$

We now consider this relation at zero frequency ($\omega = 0$). The Kramers–Kronig relations imply

$$\begin{aligned} \operatorname{Re} \chi_{ZZ}(q, 0) &= \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{d\omega'}{\omega'} \operatorname{Im} \chi_{ZZ}(q, \omega') \\ &= -\frac{C\beta}{2\pi} \int_{-\infty}^{+\infty} d\omega' S_{ZZ}(q, \omega') \\ &= -C\beta S_{ZZ}(q) \end{aligned} \qquad (21)$$

Therefore

$$\frac{1}{\epsilon(q,0)} = 1 - \frac{4\pi\, \mathrm{e}^2 C\beta}{\epsilon_0 q^2} S_{ZZ}(q) \tag{22}$$

The charge structure factor obeys sum rules. These concern the moments of order zero and of order two of the pair correlation (Stillinger and Lovett). They are

$$\lim_{q\to 0} S_{ZZ}(q) = 0$$

and

$$S_{ZZ}(q) \simeq \frac{2q^2}{\kappa^2}, \qquad q < \kappa \tag{23}$$

where

$$\kappa^2 = 8\pi\, \mathrm{e}^2 \beta C/\epsilon_0. \tag{24}$$

Equation (22) can be written in a dimensionless form. For this, we introduce a characteristic length a. Let $k = qa$. We have

$$\frac{1}{\epsilon(k,0)} = 1 - \frac{\Gamma}{k^2} S_{ZZ}(k) \tag{25}$$

where $\Gamma = \kappa^2 a^2/2$ is the coupling constant.

With Hansen and McDonald [2], we can set $a = (3/4\pi C)^{1/3}$ which implies

$$\Gamma = 3\, \mathrm{e}^2\beta/a\epsilon_0 \tag{26}$$

However, we can also choose "a" to be the distance between neighbour charges on the polyion. The coupling constant is then written ξ, and here $\xi = \mathrm{e}^2\beta/4\pi\epsilon_0 a$.

One can thus characterize polyelectrolytes by two coupling constants and this can be seen as the cause of a complex dielectric structure.

In general, the strong coupling limit (Γ, or $\xi \gg 1$) corresponds to onset of local order [1] and singular behaviour [2] in $\epsilon(\mathrm{i}q, 0)$. In polyelectrolytes, strong coupling produces "condensation", but its effect on $\epsilon(q, 0)$ is not yet explicitely derived.

4. Derivation of the structure functions in the random phase approximation

We determine the partial structure functions $S_{AB}(q)$ from the linear response functions $\chi_{AB}(q)$

$$S_{AB}(q) = -\frac{1}{\sqrt{C_A C_B \beta}} \chi_{AB}(q) \tag{27}$$

where $A(=\pm)$, $B(=\pm)$ are indices labelling the sign of the charges.

Let U_A be an external potential, acting on the charges of species A. The perturbation $\delta C_A(q)$ is the Fourier transform of the local concentration $C_A(r)$ and it can be written as

$$\left.\begin{aligned} \delta C_-(q) &= -(\chi_{--}(q)U_- + \chi_{-+}U_+) \\ \delta C_+(q) &= -(\chi_{-+}(q)U_+ + \chi_{++}U_+) \end{aligned}\right\} \tag{28}$$

The reference system from which the $\chi_{AB}(q)$ are derived, is the ideal gas. Introducing a mean field induced by charge fluctuation [10]

$$\Phi(q) = \frac{4\pi\, \mathrm{e}^2}{\epsilon_0 q^2}(\delta C_-(q) - \delta C_+(q)) \tag{29}$$

we have

$$\left.\begin{aligned} \delta C_-(q) &= -{}^\circ\chi_{--}(q)\{U_- + \Phi(q)\} \\ \delta C_+(q) &= -{}^\circ\chi_{++}(q)\{U_+ + \Phi(q)\} \end{aligned}\right\} \tag{30}$$

The ${}^\circ\chi_{AB}(q)$ are the bare response functions. They can be considered as the screened response functions.

We introduce the inverse square screening length (24) $\kappa^2 = 8\pi\, \mathrm{e}^2\beta C/\epsilon_0$ and we get

$$\chi_{AA} = {}^\circ\chi_{AA}\left\{\frac{q^2 + \kappa^{2\circ}\chi_{BB}/2\beta C}{q^2 + \kappa^2({}^\circ\chi_{AA} + {}^\circ\chi_{BB})/2\beta C}\right\} \tag{31}$$

$$\chi_{AB} = {}^\circ\chi_{AA}{}^\circ\chi_{BB}\left\{\frac{\kappa^2/2\beta C}{q^2 + \kappa^2({}^\circ\chi_{AA} + {}^\circ\chi_{BB})/2\beta C}\right\} \tag{32}$$

4.1. Simple electrolytes

Case of simple electrolytes. Here ${}^{\circ}\chi_{AA} = {}^{\circ}\chi_{BB} = \beta C$ and the partial structure factors are

$$S_{AA} = \frac{q^2 + \kappa^2/2}{q^2 + \kappa^2} = S_{BB} \tag{33}$$

$$S_{AB} = \frac{\kappa^2/2}{q^2 + \kappa^2} \tag{34}$$

The charge, number and cross correlation structure factors derived from the partial structure factors are (see Fig. 1).

$$S_{ZZ} = \frac{2q^2}{q^2 + \kappa^2} \tag{35}$$

$$S_{NN} \equiv 2, \qquad S_{ZN} \equiv 0$$

March and Tosi [1] pointed out that this system can be considered as two independent liquids respectively of charge and total concentration fluctuations.

The ionic dielectric structure function is here

$$\epsilon(q) = 1 + \kappa^2/q^2 \tag{36}$$

This relation only gives an account of the screening effect. If we include the atomic core repulsion in the calculation, eq. (35) becomes [2]

$$S_{ZZ}(q) = \frac{2q^2}{q^2\beta/C\chi_T + \kappa^2} \tag{35'}$$

where χ_T is the osmotic compressibility. This formula accounts for the competition between electric and chemical susceptibilities, which is the problem of interest.

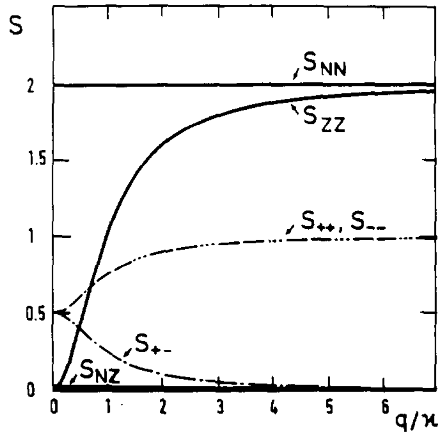

Fig. 1. Description of electrolyte structure in the frame of the random phase approximation, eqs. (33) to (35), by two equivalent sets of factors: (- - ... - -) Partial structure factors S_{++}, S_{--} and S_{+-}, and (— — —) charge, number and cross correlation structure factors S_{ZZ}, S_{ZZ} and S_{NN} are uncorrelated because $S_{HZ} \equiv 0$.

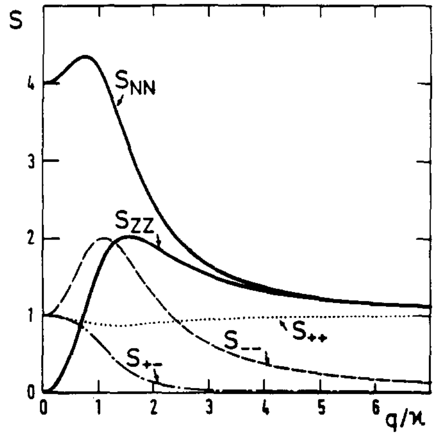

Fig. 2. Case of the disymmetric charged system. Plot of the structure factors against q, as given by eq. (37). Symbols as above. The polyion form function is assumed to be a "Debye" function, with a gyration radius $R_G = 200$ Å. The disymmetry in charge and size implies here $S_{NZ} \neq 0$. The model is unrealistic because counterion condensation is not accounted for. The true form function is not known. The charge structure factor is too important compared to the number factor.

4.2. Polyelectrolytes

The random phase approximation can be applied to polyelectrolytes in the limit of weak coupling ($\xi \ll 1$). From eqs. (31) (32) and (9) we have (see Fig. 2)

$$S_{ZZ}(q) = \frac{q^2\{N_1 h_1(q) + 1\}}{q^2 + \frac{\kappa^2}{2}\{N_1 h_1(q) + 1\}} \tag{37}$$

where the index '1' refers to the polyion: $h_1(q)$ is the polyion form function and N_1 its degree of polymerization. We assume that the counterion is a point charge.

Expanding about $q = 0$, we have here

$$S_{ZZ}(q) = \frac{2q^2}{\kappa^2} - \cdots \tag{38}$$

Equation (37) points out the importance of the polyion form function. This function modulates the dielectric response. At shorter wavelength, the charge structure function $S_{ZZ}(q)$ (definition see eq. 6) implies a different dielectric behaviour. The definition given in eq.(9) is preferable.

The situation of interest is however related to the strong coupling constant, $\xi \geqslant 1$. This generates an accumulation of counterion charges around the polyion.

5. Effects of counterion condensation

The dissymmetry in charge and molecular size in polyelectrolyte, is expected to characterize the partial structure factors, as seen in Fig. 2.

But, as already said, the main structural feature is expected to come from the high value of the coupling constant. In fact, the partial structure factors $S_{AB}(q)$ should account for the accumulation of counterion charges near the polyion. The overall behaviour is certainly different from that displayed in Fig. 2. Several effects can be qualitatively predicted:

(1) The fraction of "free" counterions is smaller than unity (about 0.3) and as a consequence the charge structure function $S_{ZZ}(q)$, eq. (9), is expected to be considerably smaller than the number structure function $S_{NN}(q)$, eq. (10). This, however, is not accounted for in Fig. 2.

(2) Accumulation of charges near the polyion induces oscillations [7] in the partial structure factor $S_{+-}(q)$, in the range $qb \geqslant 1$ where b is the diameter of the polyion. (Formula (37) is unable to account for this fact). Such oscillations will be reproduced in the charge structure factor $S_{ZZ}(q)$, and consequently in $\epsilon(q, 0)$ (see Fig. 3). Effects of charge confinement can be very strong. (For instance, charge confinement in reciprocal space induces oscillations of the dielectric constant in real space).

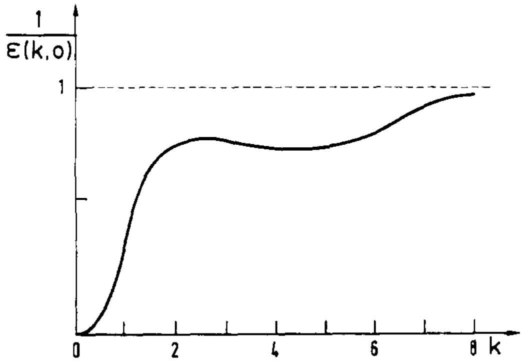

Fig. 3. Schematic plot of the inverse dielectric structure function, against reduced wave number $k = q/\kappa$. The screening effect is important in the limit $k \to 0$, the counterion confinement effect and the dipolar effect should be detectable in the range $k \geqslant 1$.

(3) Fluctuation of the condensed counterion concentration along the polyion, at fixed condensed fraction, creates electric dipoles. A dielectric increment associated with these dipoles was predicted by Oosawa [11]

$$\frac{\Delta\epsilon(q)}{\epsilon_0} = C\frac{2}{3\pi} l^3 \frac{C_+^* e^2\beta}{\epsilon_0 l} \cdot \frac{1}{q^2} \cdot \frac{1}{1 + (C_+^*/\rho) + \Phi_q} \tag{39}$$

where C_+^* is the concentration of the condensed counterions, l the length of the polyion and Φ_q the counter-counterion interaction potential.

The predicted effect is proportional to the square length l^2 of the polyion and to the condensed fraction of counterions. It contributes to increase the dielectric susceptibility.

6. Dynamics of the Brownian motion of charged molecules

The dynamics of charged molecules in aqueous solutions was investigated by Berne and Pecora [12]. Using their results (and also reference [5]), we can predict the characteristic relaxation pattern of the dynamic charge structure function

$$S_{ZZ}(q, \omega) = -\frac{2}{\beta C\omega} \operatorname{Im} \chi_{ZZ}(q, \omega) \tag{40}$$

Assuming that the bare dynamic structure function, ${}^{\circ}S(q, \omega)$, describes a Fickian diffusion characterized by a diffusion constant D

$$ {}^{\circ}S(q, \omega) = \frac{{}^{\circ}\Delta}{\omega^2 + {}^{\circ}\Delta^2} \tag{41}$$

where ${}^{\circ}\Delta = Dq^2$ then, to a first approximation

$$S_{ZZ}(q, \omega) = \frac{{}^{\circ}\Delta}{\omega^2 + {}^{\circ}\Delta^2\left(1 + \frac{\kappa^2}{q^2}\right)^2} \tag{42}$$

The corresponding half width at half maximum is

$$\omega_{1/2} = D(q^2 + \kappa^2)$$

In other words, the relaxation time associated with charge fluctuations is

$$\tau^{-1}(q) = D(q^2 + \kappa^2) \tag{43}$$

In particular, $\tau^{-1}(q)$ is non zero in the limit $q \to 0$. This limit corresponds to the overdamped plasmon frequency.

7. Discussion

We have examined the known relation between dielectric and chemical responses in charged systems. The case of electrolytes and polyelectrolytes is of particular interest because the dielectric response can be measured directly in a single scattering experiment.

The following general properties of charged macromolecular systems can be studied:

(1) In the long wavelength limit ($q \to 0$), the divergence of $\epsilon(q, 0)$ resulting from the screening of the Coulomb interaction.

(2) At shorter wavelength, the effect of the strength of the coupling constant, resulting in a local atomic ordering.

(3) The modulation of $\epsilon(q, 0)$ related to the polyion form function.

The fact that the counterion ion distribution around the polyion adjust itself in such a way that the effective coupling constant equals unity, should also have interesting consequences on the frequency dependence of $\epsilon(q, \omega)$.

In order to relate chemical and dielectric structure we have transformed the partial structure functions $S_{AB}(q)$ (A, $B = +, -$) into compound structure functions $S_{XY}(q)$ (X, $Y = Z$, N). This representation also has the advantage to describe the system in terms of "charged" and "number" liquids. It is interesting to apply this formalism to other types of mixtures such as neutral block copolymers. Their structure has similarities with the structure of charged systems. We consider first the case of an isolated diblock copolymer, for which each block has the form function $f_{1/2}(q)$. The form function of the total chain is $f(q)$. We have

$$S_{NN}(q) = f(q)$$
$$S_{ZZ}(q) = f_{1/2}(q) - f(q)$$
$$S_{NZ}(q) = 0$$

In the case of a diblock copolymer melt, we have

$$S_{NN}(q) = 0$$
$$S_{ZZ}(q) = h_{1/2}(q) - h(q)$$
$$S_{NZ}(q) = 0$$

In fact, the cross term $S_{NZ}(q)$ accounts for polydispersion. Thus, the structure of some neutral systems reproduces those of charged systems. However in the situation of interest, both short range atomic interactions and long range Coulomb interactions are combined. Scattering experiments made at zero average contrast provide data for the investigation of this problem.

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