Microscopic model of charge density distribution for critical and supercritical states of carbon

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Mass and charge density fluctuations of carbon in critical and supercritical states result in multiply charged negative and positive nanocluster ions which are the main components of the weakly ionised electronless carbon plasma.

The critical state of a single-component phase is usually described by certain parameters of 'order' (densities of mass and entropy), whose spatial fluctuations abnormally grow due to the cooperative (multi-body) nature of critical processes.[1] At high critical temperatures substances exist as a plasma, which is also characterised by charge density as an additional parameter of 'order'. Charge density fluctuations determine the electrical and optical characteristics of the medium thus stimulating considerable interest to study spatial or temporal charge density distributions, which are statistically equivalent according to the ergodic hypothesis.

It is known that a substance in a critical or supercritical state has a 'droplet-like' microstructure due to long-lived mass density fluctuations.[2] Under laser ablation of graphite, these carbon droplets were experimentally detected as charged carbon nanoclusters[3] in a gas phase by a real-time electrostatic probe technique (Figure 1), and they were also observed by scanning electron microscopy as neutral carbon nanoclusters deposited on a graphite foil surface by the laser quenching under supercritical conditions.[4] These experimental data[3,4] allow us to estimate the correlation radius R of critical density fluctuations (a characteristic size of spherical nanoclusters), which is about 10–30 nm (10^4–10^6 atoms per cluster) for a mass density of the liquid carbon phase of near 2 g cm^{-3}.[5]

The majority of physical and chemical properties of carbon nanoclusters are similar to those of a macroscopic condensed phase (*e. g.*, thermionic emission,[6] delocalisation of an excessive charge, high stability and slow growth of the consequent ionisation potentials of multiply charged ions[7]). A change in the electronic properties of carbon nanoparticles with their growth from several atoms to several hundreds of atoms results in a gradual decrease in their ionisation potential I_p and in an increase in their electron affinity E_a thus approaching the work function A_e of bulk graphite[8] for large graphite-like carbon clusters C_{60}–C_{900}.[9] Because liquid carbon is a conducting phase[10] these tendencies are described[11] by the following expressions for a conducting sphere of radius R:

$$I_\mathrm{p}(R) = A_\mathrm{e} + 0.375e^2/R \qquad (1)$$

$$E_\mathrm{a}(R) = A_\mathrm{e} - 0.625e^2/R \qquad (2)$$

The differences between I_p, E_a and A_e calculated for various graphite-like carbon nanoclusters with 10^4–10^6 atoms per cluster are very small (0.05–0.2 and 0.08–0.3 eV, respectively) as compared with the A_e value of bulk graphite (4.6 eV[12]). Due to delocalisation of an excessive charge and similar I_p and E_a values the large carbon nanoclusters can readily form multiply charged negative and positive ions.

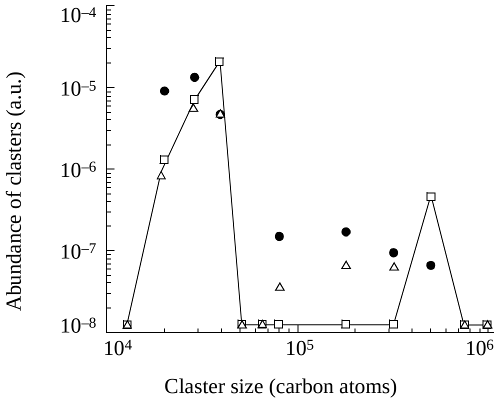

Figure 1 Dependence of the charge ($Z[C_N^{-Z}]\Delta Z$) induced on an electrostatic probe by negative nanocluster ions on the size-to-charge ratio N/Z (curve *1*); distribution (concentration $[C_N^Z]$) of nanocluster ions C_N^Z by N/Z (curve *2*); size distribution of neutral nanoclusters C_N^0 (curve *3*).

Indeed, one- or multielectron charge-transfer processes between carbon nanoclusters occur at near-critical temperatures ($kT \leq$ ≤ 1 eV).[13] The most probable process of single-electron transfer from the charged carbon nanocluster C_N^{Z1} to a charged particle M is as follows:

$$C_N^{Z1} + M^{Z2} = C_N^{Z1+1} + M^{Z2-1} \qquad (3)$$

which describes not only electron transfer between carbon nanoclusters, but also direct gas-phase ionisation of nanoclusters by collisional ionisation and thermionic emission (where M^{Z2-1} is a collisional partner or a virtual particle, respectively). The equilibrium constant of reversible process (3) is

$$K_\mathrm{p} = \frac{[C_N^{Z1+1}][M^{Z2-1}]}{[C_N^{Z1}][M^{Z2}]} = \exp\{-[I_\mathrm{p}(C_N^{Z1}) - E_\mathrm{a}(M^{Z2})]/kT\} \qquad (4),$$

where concentrations of the reacting species are placed in square brackets. It can be seen that a minimum value of a factor $[\Delta = I_\mathrm{p}(C_N^{Z1}) - E_\mathrm{a}(M^{Z2})]$ from expression (4) is favourable for direct process (3). Some characteristic values are $\Delta \approx 0$ eV for the case of single-electron transfer between carbon nanoclusters (*i.e.* $I_\mathrm{p} \approx E_\mathrm{a} \approx A_\mathrm{e}$), $\Delta > 1$ eV for the electron transfer from a nanocluster to a small positive carbon cluster ion of several atoms ($I_\mathrm{p} > 8$ eV, $E_\mathrm{a} < 3$ eV[8]) and $\Delta \approx A_\mathrm{e} = 4.6$ eV for the collisional ionisation or thermionic emission. These values indicate that a dominant channel of generalised process (3) is charging of the nanoclusters because the latter are not only effective

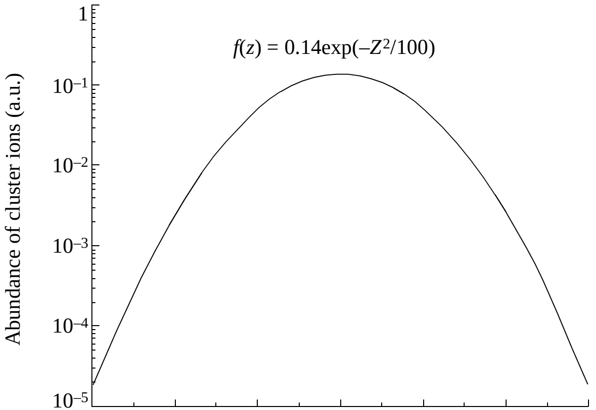

Figure 2 Charge distribution of carbon nanoclusters of $N = 5\times10^5$ atoms at $T = T_\mathrm{crit} \approx 7\times10^3$ K.

electron donors for small positive carbon cluster ions, but also effective acceptors of free electrons in a gas phase and acceptors of an excessive negative charge of small carbon cluster ions. Therefore, a critical or supercritical carbon plasma is electronless and mainly consists of positively and negatively charged nanoclusters.

The probability of consequent ionisation of a nanocluster gradually diminishes with increasing charge due to an increase in the work function of the nanocluster. The electrostatic potential of electron transfer between nanoclusters can be approximately simulated by the potential of a spherical capacitor due to a spherical symmetry of a nanocluster ionised[14]

$$U(r) = \frac{Ze}{4\pi\varepsilon_0\varepsilon}(R^{-1} - r^{-1}) \qquad (5),$$

where Z and R are the charge and the radius of the nanocluster, respectively, ε is the dielectric constant of the neutral vapour that separates the nanoclusters and ε_0 is the dielectric constant of vacuum. According to expression (5), $\Delta(Z) = eU(R)$ in (4) increases proportionally to the charge of the nanocluster C_N^Z as BZ, where the parameter B is also determined by expression (5). The abundance of multiply charged nanoclusters is not high, because equilibrium constant (4) is expressed by an exponential. For this reason, each multiply charged nanocluster mainly interacts with numerous weakly charged nanoclusters of opposite charge Zi from the surrounding 'ion atmosphere'. Thus, the yield of multiply charged nanoclusters can be expressed by the equilibrium constant of multi-step process (3)

$$\frac{[C_N^Z][M^{Zi-1}]^Z}{[C_N^0][M^{Zi}]^Z} = \exp\{-[\Delta(1) + \ldots + \Delta(Z)]/kT\} = \exp(-BZ^2/2kT) \qquad (6),$$

where the sum by the integer index Z of the nanocluster charge is placed in braces. Accounting for expression (6), the material balance equation for nanoclusters C_N with different charges is written as

$$[C_N]_\Sigma = [C_N^0]\sum_{-\infty}^{+\infty}\exp(-BZ^2/2kT) \qquad (7)$$

Thus, the resulting charge distribution $f(Z)$ of nanoclusters C_N can be presented as a normal statistical law with the continuous variable Z and parameters $\mu = 0$ and $\sigma = (kT/B)^{1/2}$

$$f(Z) = (2\pi kT/B)^{-1/2}\exp(-BZ^2/2kT) \qquad (8)$$

Equation (8), which describes normal charge density distribution for a critical (supercritical) state of carbon, is indicative of the independent character of fluctuations for this parameter of 'order'. However, there is a relationship between the parameter σ of charge density distribution and the radius R of nanoclusters (the average radius of fluctuations or correlations). For example, the maximum σ value corresponds to the critical point of a substance, where R is maximum, and B is minimum. In a supercritical region, the R value is monotonously decreased[1] with increasing T and the following increase of B results in decreasing σ in accordance with expression (8) thus suppressing the fluctuations of charge density.

Because expression (8) qualitatively describes the charge density distribution of the high-temperature critical and supercritical states of carbon, it was used for quantitative processing of time-of-flight electrostatic probe measurement data,[3] namely, the dependence of the charge induced at an electrostatic probe (collector) by gas-phase negative carbon nanoclusters on their size-to-charge ratio N/Z. In order to determine the concentrations $[C_N^Z]$ and $[C_N^0]$, the general function $I(N/Z)$ (Figure 1, curve *1*) was expanded over the range $N/Z = 10^4$–5×10^5 in a series of simple terms $Zf(Z)\Delta Z[C_N^{-1}]$ (with $\Delta Z = 1$) starting from $N/Z = 5\times10^5$, where Z was assumed to be equal to –1. The variance σ of the charge density distribution $f(Z)$ was calculated from expressions (5) and (8) using $kT = 0.6$ eV ($T \approx T_{\mathrm{crit}} \approx 7\times10^3$ K), $\varepsilon \approx 1$, $R = [(3NM_{\mathrm{at}})/(4\pi\rho_{\mathrm{liq}})]^{1/3}$ and $r = 2R[(\rho_{\mathrm{liq}}/2\rho_{\mathrm{crit}})^{1/3} - 0.5]$, where M_{at} is the mass of a carbon atom (kg), $\rho_{\mathrm{liq}} \approx 1.5\times10^3$ kg m^{-3} is the density of carbon liquid at $T < T_{\mathrm{crit}}$ and $\rho_{\mathrm{crit}} \approx 640$ kg m^{-3} is the density of carbon in the critical state.[5] The calculated σ values were equal to 3.5 and 7 for $N = 3\times10^4$ and 5×10^5 atoms, respectively. One of the resulting distributions $f(Z)$ for carbon nanoclusters of $N = 5\times10^5$ atoms is given in Figure 2.

Two main terms of the expanded function $I(N/Z)$ are related to two modes of nanoclusters centred at $N/Z = 3\times10^4$ and $N/Z = 5\times10^5$ atoms. These bimodal distributions of $[C_N^Z]$ by N/Z and $[C_N^0]$ by N are shown in Figure 1 (curves *2* and *3*). Accounting for the exponential increase in the amplitude of the specific mode of fluctuations during spinodal decomposition of a labile liquid phase,[2] we considered this bimodal distribution of carbon nanoclusters as two superimposed distributions. One distribution with $N = 5\times10^5$ atoms and $T \approx T_{\mathrm{crit}} \approx 7\times10^3$ K was well fitted by the function $I(N/Z)$ over the range of $N/Z = 8\times10^4$–5×10^5 atoms, but over the range of $N/Z = (2$–$4)\times10^4$ atoms, the experimental function $I(N/Z)$ is inconsistent with the sharp distribution at $N = 3\times10^4$ atoms and $T \approx T_{\mathrm{crit}}$. The temperature of the smaller carbon nanoclusters is much higher in accordance with the predictions of a current theory of the supercritical state[1] ($R \sim T^{-2/3}$) and can be estimated as $T \approx 2.8\times10^4$ K. This temperature of a local region in a laser-generated plasma, where spinodal decomposition of the largest carbon nanoclusters takes place, is consistent with the temperatures ($T < 3\times10^4$ K) in a near-surface 'opaqueness' region of the carbon plasma.[15]

Thus, a microscopic theory of the charge density distribution for critical and supercritical phases of carbon was developed for the first time, and an electronless character of the high-temperature plasma of negatively and positively charged carbon nanoclusters was predicted. This theory adequately describes an experimental distribution of multiply charged nanoclusters.

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