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LINE SHAPE IN THE EELS OF BINARY MIXTURES

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Using the statistical theory of the electron energy-loss spectrum (EELS) in the simple disordered systems suggested earlier by Adamian and Gerasimov, simple expressions for describing the resonance-line shape in binary mixtures were obtained for a model with binary Ornstein–Zernike correlations and a Lennard-Jones shift of the excitation energy. The reconstruction of the correlational contribution to the intensity of the energy loss near the distinctive dipole-forbidden resonance in the EELS, which takes place in the framework of the proposed model close to critical points, is discussed.

1. Introduction

It is known that electron energy-loss spectroscopy (EELS) has been a valuable technique for exploring collective electronic excitation in different systems [2]. The development of the technology of this experiment gives some hope to study the behavior of EELS close to single resonance with a width $\sim 10^{-1}$ eV, but outside of the Doppler width of a spectral line. A statistical theory of the line shape in EELS in this region for simple disordered systems was developed in [1]. It was theoretically predicted that a statistical "fine" strucure EELS due to many particle intermolecular correlations would appear. The starting point for the theory [1] is a correlational expansion method which is based on irreducible cluster expansions, in terms of many-particle distribution functions. In a system with moderate density we can use the finite length of this general correlational series and on this way one can obtain a simple expression for the cross-section of the energy loss. This question was discussed in [1, 3, 4]. At last, in [3, 4] the behavior of the line shape of the single narrow dipole-forbidden resonance near the critical point was investigated.

On the other hand, the broadening and shift of an optical spectral line caused by the interaction of the emitting (or absorbing) atoms with the

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surrounding particles in the vapors of metals and inert gases and their mixtures are commonly experimentally observed in laboratory and astronomical spectra [5]. A particularly difficult structure which includes red and violet satellites of a spectral line was experimentally observed in a large number of papers [5].

In connection with this, the aim of this paper is to extend the statistical theory of the line shape in EELS to the case of binary mixtures of simple disordered systems, where, probably, similar effects may also be reproduced, but in another scale.

It is particularly interesting to investigate the behavior of the line shape of the dipole-forbidden resonance in EELS which can be long-living near the critical point where the correlational radius tends to infinity, and for example in the case of the critical point of the phase transition the molecules of the contrary sort simply push out the coordinate sphere of the excited molecule which localizes the excitation.

It is possible to formulate a rather general theory of the pressure broadening of line profiles (like in ref. [3]) in binary mixtures (this theory will be published in the next paper), but because it is a many-body problem, it is found that the formal expressions obtained cannot be used to calculate line shapes without the introduction of some additional approximations. The nature of these approximations is determined by the molecules species and thermodynamic conditions in the system.

From this point of view we confine ourselves here to a binary correlational approximation in combination with a pair-additive Lennard-Jones model for the energy shift of a single excitation.

2. Cross-section of energy losses

The distribution of monochromatic beam of fast electrons ($E \sim 10^3$ eV) which is inelastically scattered by energy losses (ε) in the narrow, $\varepsilon \sim 10^{-2}$–10^{-1} eV, neighbourhood of a distinctive resonance with a fixed scattering angle $\theta < 1°$ in simple disordered systems of N identical, symmetrical molecules with volume V and a temperature $T \sim 10^2$ K may be simply described with the help of Born's approximation [1]. Moreover, the main contribution to the excited level is carried by the sum over the electronic states. We shall suppose that the target molecules can be considered as being in rest during the elementary act of scattering (adiabatic approximation) and that the excited level of a single molecule is degenerated. We want to emphasize that the widening of the spectral resonance due to molecular motion Δ for the parameter values of our problem $\Delta \sim 10^{-3}$–10^{-2} eV [1]. The statistical interpretation of this problem, which operates a random distribution of scattered charges, is based on the expansion of the cross section of the energy loss $I_\theta(\varepsilon)$ in a correlational series. All members of this correlational series describe irreducible contributions in $I_\theta(\varepsilon)$ due to inelastic scattering on many-particle quasi-molecular fluctuational complexes with different ranges. It is needed to stress that the correlational expansions, unlike of density power law, have a more complicated, functional character of convergence [1]. Nevertheless, in systems with moderate densities we can approximately use the finite length of the correlational series for $I_\theta(\varepsilon)$ [1, 3, 4]. For example, if we take into account only the two first terms of the correlational series for $I_\theta(\varepsilon)$, we obtain an expression, which describes the cross-section of the energy loss by scattering on a system "which consists of two-particle, fluctuational quasi-molecules", of which the regular part, as follows from [1], is equal to

$$I_\theta(\varepsilon) = \frac{1}{2}\left(\frac{e}{E\theta^2}\right)^2 n^2 \int g_2(R) \sum_{(\alpha)} Z_{\alpha,2}(\boldsymbol{q},\boldsymbol{R})\delta(\varepsilon + \mu_{\alpha,2}(\boldsymbol{R}))\,\mathrm{d}\boldsymbol{R}\,, \qquad (1)$$

where: $n = N/V$ is the number of density particles; $g_2(R)$ is the pair ("radial") distribution function;

$$Z_{\alpha,2}(\boldsymbol{q},\boldsymbol{R}) \equiv |\rho^{(2)}_{10,\alpha}(\boldsymbol{q},\boldsymbol{R})|^2\,,$$

$\rho^{(2)}_{10,\alpha}(\boldsymbol{q},\boldsymbol{R})$ is the Fourier transformation of the matrix element from the charge–density operator; the sum over α goes over the even ($\alpha = g$) and odd ($\alpha = u$) electronic states in accordance with the property of the wave function of a quasi-molecule consisting of two equal particles, accordinately, to conserve or change the sign under the inversion of electronic variables in the plane of symmetry; $\delta(Z)$ is the Dirac delta-function; $\boldsymbol{q}$ is the impulse of scattering; $\mu_{\alpha,2}(\boldsymbol{R})$ is the shift of the energy of a single excitation due to intermolecular interaction in a two-particle complex; R is the distance between two particles.

Naturally, generalization of expression (1) in the case of two-component binary mixtures leads to

$$I_\theta(\varepsilon) = \left|\frac{e}{E\theta^2}\right|^2 \left\{\frac{n_1^2}{2}\int \sum_{\alpha} Z^{(1,1)}_{\alpha,2}(\boldsymbol{q},\boldsymbol{R})\delta(\varepsilon + \mu^{(1,1)}_{\alpha,2}(\boldsymbol{R}))g_2^{(1,1)}(\boldsymbol{R})\,\mathrm{d}\boldsymbol{R} \right.$$
$$\left. + n_1 n_2 \int Z_2^{(1,2)}(\boldsymbol{q},\boldsymbol{R})\delta(\varepsilon + \mu_2^{(1,2)}(\boldsymbol{R}))g_2^{(1,2)}(\boldsymbol{R})\,\mathrm{d}\boldsymbol{R}\right\}, \qquad (2)$$

where n_1, $Z^{(i,j)}_{\alpha,2}(\boldsymbol{q},\boldsymbol{R})$, $\mu^{(i,j)}_{\alpha,2}(\boldsymbol{R})$ and $g^{(i,j)}(R)$ are partial characteristic parameters and functions which were determined vide supra but in two-component systems, indexes i, $j = 1, 2$ indicate the type of component. Integration in (2) (using the properties of the Dirac delta-function) gives

$$I_\theta(\varepsilon) = \left|\frac{e}{E\theta^2}\right|^2 n_1 \left\{ \frac{1}{2} n_1 \sum_{(\nu,\alpha)} \overline{Z^{(1,1)}_{\alpha,2}(q, R_{\nu_\alpha}(\varepsilon))}^{(\Omega)} \frac{R^2_{\nu_\alpha}(\varepsilon)}{\left|\frac{\mathrm{d}\mu^{(1,1)}_{\alpha,2}}{\mathrm{d}R}\right|_{R_{\nu_\alpha}(\varepsilon)}} g_2^{(1,1)}(R_{\nu_\alpha}(\varepsilon)) \right.$$

$$\left. + n_2 \sum_{\nu'} \overline{Z^{(1,2)}_{2}(q, R_{\nu'}(\varepsilon))}^{(\Omega)} \frac{R^2_{\nu'}(\varepsilon)}{\left|\frac{\mathrm{d}\mu^{(1,2)}_{2}}{\mathrm{d}R}\right|_{R_{\nu'}(\varepsilon)}} g_2^{(1,2)}(R_{\nu'}(\varepsilon)) \right\}. \qquad (3)$$

3. Model of localized excitation

Consider a model of two-component mixtures in which both of the components have liquid (or gaseous) ranges that overlap in some interval of thermodynamic parameters, including some neighbourhood of the critical point of phase separation.

Let us consider, for example, a situation in which the excited state of the molecule of sort number one and also the bound states of both sorts of the molecules have equal symmetry (for example S) i.e. a dipole-forbidden type of transition in the excited state.

We shall suppose also that the life-time of our distinctive dipole-forbidden resonances approximately correspond to (or are larger than) typical relaxational times for the order parameter in some neighbourhood of the critical point of phase separation, T_s (about the conditions of the existence of the localized long-living excitations in simple liquids, see for example ref. [6]). Note that, because near the critical point the intensity of long-range correlations increases, it is possible to stabilize our nonequilibrium objects (i.e. fluctuational clusters which include an excited molecule) for example with the help of a sudden transmission of our systems in the close neighbourhood of the critical point [7]. Under these determinative conditions the life-time of excitations will probably strongly increase [6, 7]. In the case of a dipole-forbidden excitation the functions of the shift $\mu^{(1,1)}_{\alpha,2}$ and $\mu^{(1,2)}_{2}$ are dependent only on the module of the correspondent interparticle distance R in both fluctuational two-particle complexes.

Let us introduce now the model in which both of these functions (which, in principle, must be calculated by means of quantum mechanics methods) will be determined in the form of a Lennard-Jones potential,

$$\mu^{(1,1)}_{\alpha,2}(R) = \frac{C^{(1,1)}_{12,\alpha}}{R^{12}} - \frac{C^{(1,1)}_{6,\alpha}}{R^{6}}\,, \qquad \mu^{(1,2)}_{2}(R) = \frac{C^{(1,2)}_{12}}{R^{12}} - \frac{C^{(1,2)}_{6}}{R^{6}}\,,$$
$$C^{(1,1)}_{12,\alpha}\,,\quad C^{(1,1)}_{6,\alpha}\,,\quad C^{(1,2)}_{12}\,,\quad C^{(1,2)}_{6} > 0\,. \tag{4}$$

At last, let us introduce the simplest Ornstein–Zernike form for a correlational function which describes order-parameter fluctuations near the critical point of a phase separation or liquid–vapor phase transitions,

$$h^{(i,j)}_2(R) = g^{(i,j)}_2(R) - 1 = A^{(i,j)}\,\frac{\mathrm{e}^{-x^{(i,j)}R}}{R}\,, \tag{5}$$

where $A^{(i,j)}$ is a proportionality constant which varies only slowly with temperature and density and $x^{(i,j)}$ is the inverse correlational radius between the molecules of different or equal species which tends to zero for corresponding correlations as a power law near the critical point of phase separation or gas–liquid phase transition (i, $j = 1, 2$).

4. EELS near the critical point

Let us investigate now the behavior of the cross section of energy loss $I_\theta(\varepsilon)$ in the small neighbourhood of distinctive dipole-forbidden resonance, particularly near the critical point of phase separation T_s, where particularly the radius of correlation between the molecules of species 1 and 2 tends to infinity (but still limited radiuses of correlations between the molecules are both of species 1, or both of species 2). From model approximations (4), (5) and (2,), (3) the next expression for $I_\theta(\varepsilon)$ follows in this case:

$$\begin{aligned}
I_\theta(\varepsilon) = {} & \left(\frac{e}{E\theta^2}\right)^2 n_1 \Bigg\{ \frac{1}{2}\, n_1 \sum_{\alpha,\nu_\alpha} \overline{Z^{(1,1)}_{\alpha,2}(q, R^{(1,1)}_{\nu_\alpha}(\varepsilon))}^{(\Omega)} \\
& \times \frac{|R^{(1,1)}_{\alpha}(\varepsilon)|^3}{|\varepsilon - C^{(1,1)}_{12,\alpha}(R^{(1,1)}_{\nu_\alpha}(\varepsilon))^{-12}|}\; g^{(1,1)}_2(R^{(1,1)}_{\nu_\alpha}(\varepsilon)) \\
& + n_2 \sum_{\nu'} \overline{Z^{(1,2)}_2(q, R^{(1,2)}_{\nu'}(\varepsilon))}^{(\Omega)}\; \frac{|R^{(1,2)}_{\nu'}(\varepsilon)|^3}{|\varepsilon - C^{(1,2)}_{12}(R^{(1,2)}_{\nu'}(\varepsilon))^{-12}|} \\
& \times \left[1 + A\,\frac{\exp(-x^{(1,2)}R^{(1,2)}_{\nu'}(\varepsilon))}{R^{(1,2)}_{\nu'}(\varepsilon)}\right]\Bigg\}\,,
\end{aligned} \tag{6}$$

where

$$R_{\nu_\alpha}^{(i,j)} = \begin{cases} \left(\dfrac{C_{6,\alpha}^{(i,j)}}{2\varepsilon}\right)^{1/6}\left[1+\delta\left(1-\dfrac{4C_{12,\alpha}^{(i,j)}}{[C_{6,\alpha}^{(i,j)}]^2}\,\varepsilon\right)^{1/2}\right]^{1/6}, & \varepsilon>0\,, \\ \left(\dfrac{C_{6,\alpha}^{(i,j)}}{2|\varepsilon|}\right)^{1/6}\left[-1+\left(1+\dfrac{4C_{12,\alpha}^{(i,j)}}{[C_{6,\alpha}^{(i,j)}]^2}\,|\varepsilon|\right)^{1/2}\right]^{1/6}, & \varepsilon<0\,, \end{cases} \tag{7}$$

and $\delta \equiv \pm 1$. It is needed to stress that in accordance with the physical meaning of $\{R_{\nu_\alpha}^{(i,j)}\}$ with the help of our model we can investigate $I_\theta(\varepsilon)$ in the interval of energy losses when $\varepsilon \in \{-\infty; \max([C_{6,\alpha}^{(i,j)}]^2/4C_{12,\alpha}^{(i,j)})\}$ only. Near the points $\{\varepsilon_{VH}\} = \{[C_{6,\alpha}^{(i,j)}]^2/4C_{12,\alpha}^{(i,j)}\}$ in EELS sharp peaks may appear. These singularities are analogous to the singularities of Van Hove for the spectral density of states.

If we deal with our model system, for example near the point of the first component liquid–vapor phase transition, with help of (3), (5) similar to (7) the following expression for $I_\theta(\varepsilon)$ can be obtained:

$$\begin{aligned} I_\theta(\varepsilon) = \left(\frac{e}{E\theta^2}\right)^2 n_1 \Bigg\{ & \frac{1}{2}\, n_1 \sum_{\alpha,\nu_\alpha} \overline{Z_{\alpha,2}^{(1,1)}(q, R_{\nu_\alpha}(\varepsilon))}^{(\Omega)} \\ & \times \frac{|R_{\nu_\alpha}^{(1,1)}(\varepsilon)|^3}{|\varepsilon - C_{12,\alpha}^{(1,1)}(R_{\nu_\alpha}^{(1,1)}(\varepsilon))^{-12}|} \left[1 + A^{(1,1)}\, \frac{\exp(-x^{(1,1)}R_{\nu_\alpha}^{(1,1)})}{R_{\nu_\alpha}^{(1,1)}(\varepsilon)}\right] \\ & + n_2 \sum_{\nu'} \overline{Z_2^{(1,2)}(q, R_{\nu'}^{(1,2)}(\varepsilon))}^{(\Omega)}\, \frac{|R_{\nu'}^{(1,2)}(\varepsilon)|^3}{|\varepsilon - C_{12}^{(1,2)}(R_{\nu'}^{(1,2)}(\varepsilon))^{-12}|} \\ & \times g_2^{(1,2)}(R_{\nu'}^{(1,2)}(\varepsilon))\Bigg\}\,. \end{aligned} \tag{8}$$

Expressions (6)–(8) on the one hand give the possibility of a direct determination of partial pair distribution functions (or parameters of a different model of them) in an individual point by measurement of the intensity of the energy losses in simple two-component disordered systems (particularly across the liquid–liquid and gas–liquid critical lines), instead of the usual procedure, which includes the inverse Fourier transform of the structure factor of scattering. This is important because due to irregular convergence of the Fourier series this last procedure is a source of inexactitudes in the determination of pair distribution functions. On the other hand, in the case of a statistically determined system, expressions (6)–(8) give the possibility of a determination of the distribution of the charge density in the neighbourhood of localized excitation in binary complexes. Let us consider now several formal limits of expressions (6)–(8), namely:

$$
\begin{aligned}
I_\theta(\varepsilon) \simeq \left(\frac{e}{E\theta^2}\right)^2 n_1 \Bigg\{ & \frac{1}{2}\, n_1 \sum_\alpha \overline{Z^{(1,1)}_{\alpha,2}(q,\infty)}^{(\Omega)} [C^{(1,1)}_{6,\alpha}]^{1/2} g_2^{(1,1)}\left(\left(\frac{C^{(1,1)}_{6,\alpha}}{\varepsilon}\right)^{1/6}\right) \varepsilon^{-3/2} \\
& + \frac{1}{2}\, n_1 \sum_\alpha \overline{Z^{(1,1)}_{\alpha,2}\left(q,\left(\frac{C^{(1,1)}_{12,\alpha}}{C^{(1,1)}_{6,\alpha}}\right)^{1/6}\right)}^{(\Omega)} \frac{(C^{(1,1)}_{12,\alpha})^{3/2}}{(C^{(1,1)}_{6,\alpha})^{5/2}}\, g_2^{(1,1)}\left(\left(\frac{C^{(1,1)}_{12,\alpha}}{C^{(1,1)}_{6,\alpha}}\right)^{1/6}\right) \\
& + n_2 \overline{Z_2^{(1,2)}(q,\infty)}^{(\Omega)} (C_6^{(1,2)})^{1/2} \\
& \times \left[1 + A^{(1,2)}\left(\frac{\varepsilon}{C_6^{(1,2)}}\right)^{1/6} \exp\left(-x^{(1,2)}\left(\frac{C_6^{(1,2)}}{\varepsilon}\right)^{1/6}\right)\right]\varepsilon^{-3/2} \\
& + n_2 \overline{Z_2^{(1,2)}\left(q,\left(\frac{C_{12}^{(1,2)}}{C_6^{(1,2)}}\right)^{1/6}\right)}^{(\Omega)} \left(\frac{C_{12}^{(1,2)}}{C_6^{(1,2)}}\right)^{1/2} \\
& \times \left[1 + A^{(1,2)}\left(\frac{C_6^{(1,2)}}{C_{12}^{(1,2)}}\right)^{1/6} \exp\left(-x^{(1,2)}\left(\frac{C_{12}^{(1,2)}}{C_6^{(1,2)}}\right)^{1/6}\right)\right]\Bigg\}\,, \\
& \varepsilon > 0\,, \quad \varepsilon \to 0 + \Delta\,,
\end{aligned} \tag{9a}
$$

$$
\begin{aligned}
I_\theta(\varepsilon) = \left(\frac{e}{E\theta^2}\right)^2 n_1 \left\{ \vphantom{\frac{1}{2}} \right. & \frac{1}{2}\, n_1 \sum_\alpha \overline{Z^{(1,1)}_{\alpha,2}\left(q,\left(\frac{C^{(1,1)}_{6,\alpha}}{2\varepsilon}\right)^{1/6}\right)}^{(\Omega)} \\
& \times \left(\frac{C^{(1,1)}_{6,\alpha}}{2}\right)^{1/2} \frac{g_2^{(1,1)}\left(\left(\dfrac{C^{(1,1)}_{6,\alpha}}{2}\right)^{1/6}\right)}{\left|1 - \dfrac{4C^{(1,1)}_{12,\alpha}}{[C^{(1,1)}_{6,\alpha}]^2}\,\varepsilon\right|}\, \varepsilon^{-3/2} \\
& + n_2 \overline{Z_2^{(1,2)}\left(q,\left(\frac{C_6^{(1,2)}}{2\varepsilon}\right)^{1/6}\right)}^{(\Omega)} \left(\frac{C_6^{(1,2)}}{2}\right)^{1/2} \\
& \times \frac{1 + A^{(1,2)}\left(\dfrac{2\varepsilon}{C^{(1,2)}_{6,\alpha}}\right)^{1/6} \exp\left(-x^{(1,2)}\left(\dfrac{C^{(1,2)}_{6,\alpha}}{2\varepsilon}\right)^{1/6}\right)}{\left|1 - \dfrac{4C_{12}^{(1,2)}}{[C_6^{(1,2)}]^2}\,\varepsilon\right|}\, \varepsilon^{-3/2} \left. \vphantom{\frac{1}{2}} \right\}, \\
& \varepsilon > 0\,, \quad \varepsilon \to \{\varepsilon_{\mathrm{VH}}\}\,,
\end{aligned} \tag{9b}
$$

$$\begin{aligned} I_\theta(\varepsilon) = {} & \left(\frac{e}{E\theta^2}\right)^2 n_1 \left\{ \frac{1}{2}\, n_1 \sum_\alpha \overline{Z^{(1,1)}_{\alpha,2}\left(q, \left(\frac{C^{(1,1)}_{12,\alpha}}{C^{(1,1)}_{6,\alpha}}\right)^{1/6}\right)}^{(\Omega)} \right. \\ & \times \left(\frac{C^{(1,1)}_{12,\alpha}}{C^{(1,1)}_{6,\alpha}}\right)^{3/2} \frac{1}{C^{(1,1)}_{6,\alpha}}\, g_2^{(1,1)}\left(\left(\frac{C^{(1,1)}_{12,\alpha}}{C^{(\alpha)}_6}\right)^{1/6}\right) \\ & + n_2 \overline{Z_2^{(1,2)}\left(q, \left(\frac{C^{(1,2)}_{12}}{C^{(1,2)}_6}\right)^{1/6}\right)}^{(\Omega)} \frac{(C^{(1,2)}_{12})^{3/2}}{(C^{(1,2)}_6)^{5/2}} \\ & \left. \times \left[1 + A^{(1,2)}\left(\frac{C^{(1,2)}_6}{C^{(1,2)}_{12}}\right)^{1/6} \exp\left(-x^{(1,2)}\left(\frac{C^{(1,2)}_{12}}{C^{(1,2)}_6}\right)^{1/6}\right)\right]\right\} . \\ & \varepsilon < 0 , \quad |\varepsilon| \to 0 + \Delta , \end{aligned} \tag{9c}$$

$$\begin{aligned} I_\theta(\varepsilon) = {} & \left(\frac{e}{E\theta^2}\right)^2 n_1 \left\{ \frac{1}{2}\, n_1 \sum_\alpha \overline{Z^{(1,1)}_{\alpha,2}\left(q, \left(\frac{C^{(1,1)}_{12,\alpha}}{|\varepsilon|}\right)^{1/12}\right)}^{(\Omega)} \right. \\ & \times (C^{(1,1)}_{12,\alpha})^{1/4} g_2^{(1,1)}\left(\left(\frac{C^{(1,1)}_{12,\alpha}}{|\varepsilon|}\right)^{1/12}\right)|\varepsilon|^{-13/12} \\ & + n_2 \overline{Z_2^{(1,2)}\left(q, \left(\frac{C^{(1,2)}_{12}}{|\varepsilon|}\right)^{1/12}\right)}^{(\Omega)} (C^{(1,2)}_{12})^{1/4} \\ & \left. \times \left[1 + A^{(1,2)}\left(\frac{|\varepsilon|}{C^{(1,2)}_{12}}\right)^{1/12} \exp\left(-x^{(1,2)}\left(\frac{C^{(1,2)}_{12}}{|\varepsilon|}\right)^{1/12}\right)\right]|\varepsilon|^{-13/12}\right\} , \\ & \varepsilon < 0 , \quad |\varepsilon| \to \infty . \end{aligned} \tag{9d}$$

As follows from (9) the spectral line is strongly asymmetric and the velocity of changing of the $I_\theta(\varepsilon)$ in stokes and anti-stokes neighbourhoods of resonances is different. Elementary analysis of (9) shows that the EELS near the single dipole-forbidden resonances has a complex behavior and is strongly dependent on the distances to the critical points, values of the spectral intervals of energy losses close to impact core Δ, concentrations of the molecules both of species 1 and 2.

It is stressed, that if all $\{C^{(i,j)}_{12,\alpha}\} \to 0$, the anti-stokes neighbourhood of resonance simply disappears, and in neglecting the correlational effects ($g_2^{(i,j)} \approx 1$) we obtain that $I_\theta^{(0)}(\varepsilon) \sim \varepsilon^{-3/2} + \text{const}$. Besides, the numerical value of the constant in this expression (and in (9)) depends on relative concentrations of the molecules of both species.

For investigation of the behavior, particularly of the correlational contribution $I_\theta^{(\text{corr})}(\varepsilon)$ in the total cross section of energy loss $I_\theta(\varepsilon)$, let us introduce the spectral density of states [see ref. [3]); $N(\varepsilon) = I_\theta(\varepsilon)/I_\theta^{(0)}(\varepsilon)$, $N^{(\mathrm{corr})}(\varepsilon) = I_\theta^{(\mathrm{corr})}(\varepsilon)/I_\theta^{(0)}(\varepsilon)$ ($N(\varepsilon) = 1 + N^{(\mathrm{corr})}(\varepsilon)$). Here $I_\theta^{(0)}(\theta)$ means the cross section of energy loss in "ideal-gas two-component mixtures" in neglecting the interparticle correlations (within the framework of a model with the van der Waals shift of energy of the single excitation). By definition, $N(\varepsilon)$ ($N^{(\mathrm{corr})}(\varepsilon)$) describes the difference in behavior of $I_\theta(\varepsilon)$ ($I_\theta^{(\mathrm{corr})}(\varepsilon)$) in relation to $I_\theta^{(0)}(\varepsilon)$. For simplicity we shall suppose in what follows that the difference between even (g) and odd (u) terms is negligible (particularly, it means that $C_{6,\mathrm{g}}^{(i,j)} \simeq C_{6,\mathrm{u}}^{(i,j)} \equiv C_6^{(i,j)}$, $C_{12,\mathrm{g}}^{(i,j)} \simeq C_{12,\mathrm{u}}^{(i,j)} \equiv C_{12}^{(i,j)}$). Within the framework of approximations which were adopted, with help of (9), we obtain

$$\begin{aligned} N(\varepsilon) = 1 &+ a(n_1, n_2, T)\varepsilon \cos\left(\frac{\tilde{\beta}^{(1,1)}}{\varepsilon^{1/6}}\right) \exp\left[-\frac{\tilde{x}^{(1,1)}}{\varepsilon^{1/6}}\right] \\ &+ b(n_1, n_2, T)\varepsilon^{1/6} \exp\left[-\frac{\tilde{x}^{(1,2)}}{\varepsilon^{1/6}}\right] + C(n_1, n_2, T)\varepsilon^{3/2}, \\ &\varepsilon > 0, \quad \varepsilon \to 0 + \Delta, \end{aligned} \tag{10a}$$

$$\begin{aligned} N(\varepsilon) = 1 + \Bigg[& n_1 \Gamma_1^{(1,1)}(2\varepsilon) h_2^{(1,1)}\left(\left(\frac{C_6^{(1,1)}}{2\varepsilon}\right)^{1/6}\right) \Big/ |1 - \varepsilon/\varepsilon_{\mathrm{VH}}^{(1)}| \\ &+ n_2 \Gamma_1^{(1,2)}(2\varepsilon)\left(\frac{2\varepsilon}{C_6^{(1,2)}}\right)^{1/6} A^{(1,2)}(n_1, n_2, T) \\ &\times \exp\left(-\frac{x^{(1,2)}}{(2\varepsilon)^{1/6}}\right) \Big/ |1 - \varepsilon/\varepsilon_{\mathrm{VH}}^{(2)}| \Bigg] \\ & /[n_1 \Gamma_1^{(1,1)}(2\varepsilon)/|1 - \varepsilon/\varepsilon_{\mathrm{VH}}^{(1)}| + n_2 \Gamma_1^{(1,2)}(2\varepsilon)/|1 - \varepsilon/\varepsilon_{\mathrm{VH}}^{(2)}|], \\ & \varepsilon > 0, \quad \varepsilon \to \{\varepsilon_{\mathrm{VH}}^{(i)}\}, \quad i = 1, 2, \end{aligned} \tag{10b}$$

$$\begin{aligned} N(\varepsilon) = 1 + \Bigg[& n_1 \Gamma_2^{(1,1)} h_2^{(1,1)}\left(\left(\frac{C_{12}^{(1,1)}}{C_6^{(1,1)}}\right)^{1/6}\right) \\ &+ n_2 \Gamma_2^{(1,2)}\left(\frac{C_6^{(1,2)}}{C_{12}^{(1,2)}}\right)^{1/6} A^{(1,2)}(n_1, n_2, T) \\ &\times \exp\left(-x^{(1,2)}\left(\frac{C_{12}^{(1,2)}}{C_6^{(1,2)}}\right)^{1/6}\right) \Bigg] \\ & /[n_1 \Gamma_2^{(1,1)} + n_2 \Gamma_2^{(1,2)}], \\ & \varepsilon < 0, \quad |\varepsilon| \to 0 + \Delta, \end{aligned} \tag{10c}$$

$$\begin{aligned} N(\varepsilon) = 1 + \Bigg[& n_1 \Gamma_3^{(1,1)}(|\varepsilon|) h_2^{(1,1)}\left(\left(\frac{C_{12}^{(1,1)}}{|\varepsilon|}\right)^{1/12}\right) \\ & + n_2 \Gamma_3^{(1,2)}(|\varepsilon|) \left(\frac{|\varepsilon|}{C_{12}^{(1,2)}}\right)^{1/12} A^{(1,2)}(n_1, n_2, T) \\ & \times \exp\left(-x^{(1,2)}\left(\frac{C_{12}^{(1,2)}}{|\varepsilon|}\right)^{1/12}\right)\Bigg] \\ & /[n_1 \Gamma_3^{(1,1)}(|\varepsilon|) + n_2 \Gamma_3^{(1,2)}(|\varepsilon|)] , \\ & \quad \varepsilon < 0 , \quad |\varepsilon| \to \infty , \end{aligned} \tag{10d}$$

where

$$\begin{aligned} a(n_1, n_2, T) &= [C_6^{(1,1)}]^{-1/6} \frac{n_1 \Gamma_1^{(1,1)}(\Delta)}{n_1 \Gamma_1^{(1,1)}(\Delta) + n_2 \Gamma_1^{(1,2)}(\Delta)} A^{(1,1)}(n_1, T) , \\ b(n_1, n_2, T) &= [C_6^{(1,2)}]^{-1/6} \frac{n_2 \Gamma_1^{(1,2)}(\Delta)}{n_1 \Gamma_1^{(1,1)}(\Delta) + n_2 \Gamma_1^{(1,2)}(\Delta)} A^{(1,2)}(n_1, n_2, T) , \\ c(n_1, n_2, T) &= \Bigg[n_1 \Gamma_2^{(1,1)} h_2^{(1,1)}\left(\left(\frac{C_{12}^{(1,1)}}{C_6^{(1,1)}}\right)^{1/6}\right) \\ & \qquad + n_2 \Gamma^{(1,2)} \left(\frac{C_6^{(1,2)}}{C_{12}^{(1,2)}}\right)^{7/6} C_6^{(1,2)} A^{(1,2)}(n_1, n_2, T) \\ & \qquad \times \exp\left(x^{(1,2)}\left(\frac{C_{12}^{(1,2)}}{C_6^{(1,2)}}\right)^{1/6}\right)\Bigg] \\ & \qquad /(n_1 \Gamma^{(1,1)}(\Delta) + n_2 \Gamma^{(1,2)}(\Delta)) , \end{aligned}$$

$$\tilde{\beta}^{(1,1)} = \beta^{(1,1)}(C_6^{(1,1)})^{1/6} , \qquad \tilde{x}^{(i,j)} = x^{(i,j)}(C_6^{(i,j)})^{1/6} , \quad i, j = 1, 2 , \tag{11}$$

$$\Gamma_1^{(i,j)}(\Delta) = \tau_{ij} \overline{Z_2^{(i,j)}\left(q, \left(\frac{C_6^{(i,j)}}{\Delta}\right)^{1/6}\right)}^{(\Omega)} , \qquad \tau_{11} = \tfrac{1}{2} , \quad \tau_{12} = 1 ,$$

$$\Gamma_2^{(i,j)} = \tau_{ij} \overline{Z_2^{(i,j)}\left(q, \left(\frac{C_{12}^{(i,j)}}{C_6^{(i,j)}}\right)^{1/6}\right)}^{(\Omega)} ,$$

$$\{\varepsilon_{\mathrm{VH}}^{(i)}\} = \frac{[C_6^{(1,i)}]^2}{4 C_{12}^{(1,i)}} , \qquad i = 1, 2 ,$$

$$\Gamma_3^{(i,j)}(|\varepsilon|) = \tau_{ij} \overline{Z_2^{(i,j)}\left(q, \left(\frac{C_{12}^{(i,j)}}{|\varepsilon|}\right)^{1/12}\right)}^{(\Omega)} (C_{12}^{(i,j)})^{1/4} .$$

Note that in (10) we have carried out the correspondent limit transitions also for function $I_{\theta}^{(0)}(\varepsilon)$. Also note that in (10) we used the next asymptotic form for $h_2^{(1,1)}(Z)$, when $Z \to \infty$ [8]:

$$h_2^{(1,1)}(Z) \sim \frac{A^{(1,1)}(n_1, T)}{Z} \exp(-x^{(1,1)} Z) \cos(\beta^{(1,1)} Z + \delta^{(1,1)}) , \quad (12)$$

where $A^{(1,1)}$, $x^{(1,1)}$, $\beta^{(1,1)}$ and $\delta^{(1,1)}$ are constants.

From (10)–(12) it follows that in the fixed neighbourhood of the critical point of phase separation ($x^{(1,2)} \neq 0$) scaling behavior of the correlational contribution in relation to the "ideal gas mixture" limit, approximately, takes place near the impact core Δ in the stokes neighbourhood and also in the asymptotic region of anti-stokes neighbourhood of single resonance, i.e.

$$N(\varepsilon) \simeq 1 + \begin{cases} C(n_1, n_2, T)\varepsilon^{3/2} , & \varepsilon > 0 , \quad \varepsilon \to 0 + \Delta , \\ \dfrac{n_1 \Gamma_3^{(1,1)}(\pi)}{n_1 \Gamma_3^{(1,1)}(\infty) + n_2 \Gamma_3^{(1,2)}(\infty)} h_2^{(1,1)}(0) & \\ \quad + \dfrac{n_2 \Gamma_3^{(1,2)}(\infty)}{n_1 \Gamma_3^{(1,1)} + n_2 \Gamma_3^{(1,2)}(\infty)} A^{(1,2)}(n_1, n_2, T)|\varepsilon|^{1/12} , & \\ & \varepsilon < 0 , \quad |\varepsilon| \to \infty . \end{cases} \quad (13)$$

Stressed that with help of (13), in principle, we obtain the possibility of direct determination of $h_2^{(1,1)}(0)$ (or $g_2^{(1,1)}(0)$), and the behavior of $h_2^{(1,1)}(R)$ ($g_2^{(1,1)}(R)$) on a small distance R.

Then in the neighbourhood of Van Hove's singularities both types $\{\varepsilon_{\mathrm{VH}}^{(i)}\}$ of scaling behavior disappear, namely

$$N(\varepsilon) \simeq 1 + \begin{cases} h_2^{(1,1)}\left(\left(\dfrac{C_6^{(1,1)}}{2\varepsilon}\right)^{1/16}\right) , & \varepsilon \to \varepsilon_{\mathrm{VH}}^{(1)} , \\ \left(\dfrac{2\varepsilon}{C_6^{(1,2)}}\right)^{1/6} A^{(1,2)}(n_1, n_2, T) \exp\left(-\dfrac{x^{(1,2)}}{(2\varepsilon)^{1/6}}\right) , & \varepsilon \to \varepsilon_{\mathrm{VH}}^{(2)} . \end{cases} \quad (14)$$

As follows from (14) we obtain that the density of state in the narrow stokes neighbourhood of the different types of Van Hove points have a different behavior (in the case of the first type Van Hove's point oscillation takes place).

At last, the anti-stokes impact core neighbourhood is practically constant and it depends only on the thermodynamic state of the system. The limit transition $x^{(1,2)} \to 0$ as follows from (14) induces scaling behavior of $N(\varepsilon)$ also close to second type Van Hove points, i.e. $N(\varepsilon) \simeq 1 +$

$(2\varepsilon/C_6^{(1,2)})^{1/6}A^{(1,2)}(n_1, n_2, T_s)$. It is interesting to stress that the correlational structure of EELS in the stokes neighbourhood near the impact core of single resonance close to the critical point has a complex nonmonotonic behavior and in the double limit $x^{(1,2)} \to 0$, $\varepsilon \to 0 + \Delta$ the index of the power law changes which describes scaling, in accordance with the next rule:

$$\begin{aligned} N(\varepsilon) \simeq\; & 1 + a(n_1, n_2, T)\varepsilon \cos \frac{\tilde{\beta}^{(1,1)}}{\varepsilon} \exp\left(-\frac{\tilde{x}^{(1,1)}}{\varepsilon^{1/6}}\right) \\ & + b(n_1, n_2, T)\varepsilon^{1/6} \exp\left(-\frac{\tilde{x}^{(1,2)}}{\varepsilon^{1/6}}\right) \\ & + c(n_1, n_2, T)\varepsilon^{3/2} \to c(n_1, n_2, T)\varepsilon^{3/2}, \\ & \varepsilon > 0, \quad \varepsilon \to 0 + \Delta, \quad x^{(1,2)} \neq 0, \end{aligned} \tag{15a}$$

$$\begin{aligned} N(\varepsilon) \simeq\; & 1 + a(n_1, n_2, T)\varepsilon \cos \frac{\tilde{\beta}^{(1,1)}}{\varepsilon} \exp\left(-\frac{\tilde{x}^{(1,1)}}{\varepsilon 1/6}\right) \\ & + b(n_1, n_2, T)\varepsilon^{1/6} + c(n_1, n_2, T)\varepsilon^{3/2} \\ & \to b(n_1, n_2, T_c)\varepsilon^{1/6} + c(n_1, n_2, T_c)\varepsilon^{3/2} \to b(n_1, n_2, T_c)\varepsilon^{1/6}, \\ & \varepsilon > 0, \quad \varepsilon \to 0 + \Delta, \quad x^{(1,2)} \to 0. \end{aligned} \tag{15b}$$

Thus, close to the impact core in the different neighbourhoods of single dipole-forbidden resonances near the critical point of phase separation, at first, nonmonotonic, then two-index and at last one-index scaling behavior of correlational contribution in $I_\theta(\varepsilon)$ takes place. Similar expressions can be obtained with the help of (8) in the case of critical point gas–liquid types (see ref. [4]).

Thus, in the narrow stokes neighbourhoods of distinctive dipole-forbidden resonance which is formed by a long-range interparticle correlation an essential change of correlational structure of the EELS takes place particularly close to the critical point of phase separation where the corresponding correlational radius tends to infinity. Contrary, in the asymptotic anti-stokes neighbourhood of the single resonance the correlational contribution (which is formed due to short-range correlation) is naturally practically independent from the critical behavior of the system target.

Note that on a way of fracton interpretation of the spectral density of states in the EELS [3], as follows from (13)–(15), fracton dimension $\bar{\bar{d}}$, which describes the scaling behavior of the correlational contribution: $N(\varepsilon) \sim \varepsilon^{\bar{\bar{d}}-1}$, changes not only in the different neighbourhoods of the critical point, but also in the different neighbourhoods of the single dipole-forbidden resonance and belongs to the interval [1. 17; 2. 5]. It means that fractal sets, if they appear in the tasks about the line shape in the EELS (two-particle fluctuational clusters which include an excited molecule play a role of localized fractal object fractons), have a spectrum of scaling indexes (see, also ref. [9]).

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References

[1] V.M. Adamian and O.I. Gerasimov, Ukrainsky Fisichesky Journal (USSR) 27 (1982) 935; in: Spectrum of Electron Energy Loss in Disordered Systems (ITF, Kiev, 1985); Teoreticheskaia i Matematicheskaia Fiska (USSR) 74 (1987) 412.
[2] K. Sturm, Adv. in Phys. 31 (1982) 1.
A.A. Lucas and others, Int. Quant. Chem. 19 (1986) 687.
M. Liehz and others, Phys. Rev. B 33 (1986) 5682.
[3] O.I. Gerasimov and V.M. Adamian, Phys. Rev. A (1988), to be published, preprint KUL-MF-87/03 (1987).
[4] O.I. Gerasimov, Europhys. Lett. (1988), to be published, preprint KUL-MF-87/05 (1987).
[5] J. Szudy and W.E. Baylis, J. Quant. Spectr. Radiat. Transfer. 15 (1975) 641.
C. Peach, Adv. in Phys. 30 (1981) 367.
N. Allard and J. Kielkopf, Rev. Mod. Phys. 54 (1982) 1103.
C. Peach, J. Phys. B: At. Mol. Phys. 17 (1984) 2599; 20 (1987) 1175.
[6] H.T. Davis and R. Brown, Low-energy electrons in nonpolar fluids, in: Advances in Chemical Physics (Wiley, New York, 1975).
S.A. Rice, J. Chem. Phys. 44 (1966) 4470.
S. Watanabe, J. Phys. Soc. Japan 54 (1985) 1665.
T. Matsuo, N. Kobayashi and Y. Kaneko, J. Phys. Soc. Japan 56 (1987) 13.
[7] K. Binder and D.W. Heerman, Growth of domains and scaling in the late stages of phase separation, in: Scaling Phenomena in Disordered Systems, R. Pynn and A. Skjeltorp, eds. (Plenum, New York, 1985).
[8] N.H. March and M. Parinello, Collective Effects in Solids and Liquids (Adam Hilger, Bristol, 1982).
[9] M. Jensen, L. Kadanoff and I. Procaccia, Phys. Rev. A 36 (1987) 1409.