Diagram technique for finding of vertex functions in the Landau theory of heteropolymer liquids

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Abstract. The problem on finding the coefficients of the Landau free energy expansion into the power series of parameter of order has been considered for solutions and melts of linear heteropolymers whose molecules comprise several types monomeric units arranged stochastically. The presence of such a quenched structural disorder places this problem outside the framework of the traditional statistical physics inviting for its solution special approaches. One of them, based on the replica concept and actively engaged in theoretical physics of disordered systems, has been invoked in this paper to derive expressions for the vertex functions in the Landau theory of heteropolymer liquids. An algorithm has been formulated which permits one resorting to the simple diagram technique to write down expressions for these functions of any order in terms of the statistical characteristics of chemical quenched structure of polymer molecules. Explicit expressions for the contributions to the Landau free energy up to the fourth degree of order parameters for polymer systems with an arbitrary structural disorder have been presented to illustrate this general algorithm. Its potentialities have been also exemplified for the melt of random m-component copolymer where exact analytical formulas for these contributions up to $n = 6$ at an arbitrary m have been derived for the first time.

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1 Introduction

The Landau mean-field theory is one of the principal approaches in studying structural phase transitions in condensed matter theory [1]. The essence of this approach consists in expanding non-equilibrium free energy $\mathcal{F}$ into the power series of parameter of order ψ and neglecting all its terms except the first few. Such a truncation of the series is quite correct in the vicinity of the critical point where the values of ψ are small. To find the equilibrium value of the free energy F in the framework of the Landau theory it is necessary to minimize $\mathcal{F}$ with respect to ψ.

A special theoretical consideration is employed when examining transitions into incommensurable phases [1–3]. Here parameter of order $\psi(\mathbf{r})$ is specified on the continuum of points $\mathbf{r}$ of three-dimensional Euclidian space, whereas the Landau free energy $\mathcal{F}$ represents the functional series rather than the ordinary one. In momentum representation this series coefficients known as vertex functions depend on wave vector $\mathbf{q}$ viewed as a continuous variable. The character of this dependence is predetermined by the system's peculiarities at the molecular

level, and thus vertex functions can be found only by resorting to the microscopic theory. Elaborating such a theory for solutions and melts of polymers whose molecules comprise more than one type of monomeric units one inevitably comes up against fundamental difficulties. This is because real heteropolymer liquids consist of enormous (virtually infinite) number of types of molecules, differing in chemical composition and structure. Averaging over such a quenched structural disorder complicates qualitatively the determination of the equilibrium characteristics of these liquids. For the solution of this kind of problems the necessity arises of invoking rather sophisticated specific methods of the statistical physics of disordered systems, for instance, the replica trick [4,5]. The replica formalism, traditionally used to find the free energy of such systems [5–7] can be also employed to derive expressions of vertex functions appearing in the Landau theory. This statement, which is of prime importance for the theory of disordered systems, is exemplified in the present work by the consideration of a heteropolymer liquid containing linear macromolecules with an arbitrary distribution of different type monomeric units along polymer chains. Since here we consider the melt of random heteropolymers rather than single polymer chain with random volume

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interactions, there is no need to resort to spin glass analogue of the order parameter used in works devoted to the problem of the protein folding [8,9].

There is a number of publications in literature reporting the solution of the problem of finding the expressions for order 2, 3, 4 vertex functions for bi- and three-block copolymers [10–17], gradient copolymers [18], multiblock copolymers [19–24], and statistical copolymers whose chemical structure is either random [25,26] or describable by the Markov chain [27–34]. Authors of the vast majority of these papers studied exclusively binary copolymers resorting therewith to some assumptions, such as liquids' incompressibility and/or the infinite length of its constituent macromolecules. That is why of fundamental theoretical interest is the development of a general algorithm enabling one to find the vertex functions of any order for arbitrary linear copolymers with any number of types of monomeric units.

Such an algorithm, free from the above assumptions, was put forward by the authors of paper [29]. There a procedure was formulated providing the possibility to express the vertex functions through certain statistical characteristics of the chemical structure of copolymer chains. As a matter of convenience for practical realization of this procedure it was suggested to resort to the diagram technique, analogous to that generally used in the theory of phase transitions [35,36]. One of the major advantages of this approach is that, when employed to design computer programs for the construction of phase diagrams of heteropolymer liquids, it permits a tedious procedure of writing down and programming highly cumbersome analytical expressions to be skipped. The diagram technique [35] has a limited applicability being designed exclusively for finding just those vertex functions (referred to as local ones [27,37]) which are needed to determine the cloud point curve, spinodal and critical points. To calculate other elements of a phase diagram of polydisperse heteropolymer liquids in the framework of the Landau theory it is necessary to find other vertex functions (termed non-local ones [27,37]). They are absent under theoretical consideration of traditional systems comprising only low-molecular weight components as well as hypothetical monodisperse heteropolymer liquids consisting of identical macromolecules. However for examination of the thermodynamics of real heteropolymers showing a strongly pronounced polydispersity, nonlocal vertices were found to play a decisive role [38]. This stipulates the importance of developing a diagram technique for their determination. Some hints as to how this problem can be approached are provided in papers [37,38]. However, the authors restricted their consideration to the simplest of the nonlocal vertex functions whose order is four. In the present paper a diagram technique extending that introduced earlier [37,38] is outlined. It enables one to find both local and nonlocal vertex functions for the solutions and melts of linear heteropolymers with arbitrary chemical structure.

The paper is organized as follows. Firstly, the problem is stated to the solution of which this paper is devoted to and the functionals used for this solution are discussed.

Then elements of the diagram technique are introduced and general rules of its application for establishing the relation between the Fourier transforms of vertex functions and the Fourier transforms of physical correlation functions are formulated. After that an algorithm is set forth that permits to express these latter through generating functions of chemical correlators characterizing the chemical structure of macromolecules. The potentialities of the general approach put forward in the last section for finding vertex functions of order $n > 4$ unknown in literature so far are exemplified for a random copolymer. Three Appendices conclude the paper which provide a rigorous substantiation of the algorithm underlying the introduced diagram technique and present expressions for different order contributions into the Landau free energy of heteropolymer liquids derived by this technique.

2 General treatment

Let us examine an arbitrary polymer liquid that consists of linear molecules varying in numbers $l_1, \ldots, l_\alpha, \ldots, l_m$ of monomeric units of different types $M_1, \ldots, M_\alpha, \ldots, M_m$ and in the pattern of their arrangement in polymer chains. Among such liquids are melts and solutions of linear heteropolymers. It goes without saying that the general theoretical framework embraces molecules of homopolymers and solvents. The thermodynamically equilibrium state of a polymer system under the mean field theory consideration is characterized by density spatial distributions $\{\rho_\alpha(\mathbf{r})\}$ of monomeric units and solvent molecules of every type. Let us denote overall number of both of them by M. Unlike the second ones which are true thermodynamic components of a polymer system, the first ones represent quasicomponents. Since monomeric units in a macromolecule are linked by stable covalent bonds, the notion of the chemical potential makes no physical sense for them. This circumstance is responsible for a number of qualitative peculiarities arising under the elaboration of the Landau theory for polymer liquids. When developing such a theory we will proceed from the Lifshitz concept [39] by which the free energy of a polymer liquid is presented as a sum of two auxiliary subsystems. The first of them, subsystem of "separate units" (SU), is a liquid whose thermodynamic components are solvent molecules and monomeric units M_α. The second one, referred to as subsystem of "chemical bonds" (CB), is the ideal gas of macromolecules and solvent molecules. In accordance with the Lifshitz concept rigorously substantiated in polymer physics [39], the Landau free energy, divided by overall number M of minimal structural units, can be written down as the difference of two functionals

$$\Delta\mathcal{F}\{[\rho_\alpha]\} = \mathcal{F}^*\{[\rho_\alpha]\} - T\mathcal{S}_L\{[\rho_\alpha]\} \qquad (1)$$

The first of them

$$\mathcal{F}^*\{[\rho_\alpha]\} = \mathcal{F}_{SU} - \mathcal{F}_{IG} = \frac{1}{M}\int f^*(\rho_\alpha(\mathbf{r}))d\mathbf{r} \qquad (2)$$

represents the difference of partial free energies of the subsystem of separate units $\mathcal{F}_{SU}$ and ideal gas of these

units $\mathcal{F}_{SU}$ at fixed densities' distributions $\{\rho_\alpha(\mathbf{r})\}$. Function f^* within the framework of the Lifshitz concept is believed to be known from a theory of low-molecular weight liquid. Particularly, in the "lattice liquid" model it reads

$$\frac{f^*(\{\Phi_\alpha\})v}{T} = (1-\Phi)\ln(1-\Phi) + \Phi - \frac{1}{T}\sum_{\alpha\beta}\epsilon_{\alpha\beta}\Phi_\alpha\Phi_\beta \quad (3)$$

where volume fraction $\Phi_\alpha(\mathbf{r})$ of α-th minimal type structural units at point $\mathbf{r}$ is related with their density at this point in a simple way $\Phi_\alpha(\mathbf{r}) = v\rho_\alpha(\mathbf{r})$. This model parameters are volume v of an elementary cell of the lattice and the matrix of physical interactions between units. Its element $\epsilon_{\alpha\beta}$ equals the energy of the formation of a contact between units M_α and M_β. Quantity $\Phi = \Phi_1 + \ldots + \Phi_m$ can, generally speaking, be dependent on $\mathbf{r}$. Its average value $\Phi = \bar{\rho}v = V_{min}/V$ is equal to the ratio of minimal volume $V_{min} = Mv$, which could be occupied by M units under their most compact packing, to volume V they occupy in reality. The second functional in the right-hand side of expression (1), named the partial "Lifshitz entropy" [39,40] is defined by relationship

$$\mathcal{S}_L\{[\rho_\alpha]\} = \frac{1}{M}\sum_\alpha \int d\mathbf{r} h_\alpha(\mathbf{r})\rho_\alpha(\mathbf{r}) - \frac{1}{T}\mathcal{F}_{CB}\{[h_\alpha]\}. \quad (4)$$

The second term in the right-hand side of this expression is the partial free energy of a CB subsystem situated in external fields $H_\alpha(\mathbf{r}) = Th_\alpha(\mathbf{r})$ ($\alpha = 1, \ldots, m$). Extremal values of dimensionless fields $\{h_\alpha(\mathbf{r})\}$ can be found in the mean field approximation from the following set of equations

$$\rho_\alpha(\mathbf{r}) = \frac{M}{T}\frac{\delta\mathcal{F}_{CB}\{[h_\alpha]\}}{\delta h_\alpha(\mathbf{r})}, \quad (\alpha = 1, \ldots, m). \quad (5)$$

According to the general algorithm underlying the Landau theory [1], one is supposed to expand functional $\Delta\mathcal{F}\{[\rho_\alpha]\}$ (1) into the functional series in powers of small order parameters $\{\psi_\alpha(\mathbf{r})\}$ restricting the expansion to several first terms. With the calculation of thermodynamic characteristics of real systems in mind it is convenient to determine α-th order parameter via expression $\psi_\alpha(\mathbf{r}) = (\rho_\alpha(\mathbf{r}) - \bar{\rho}_\alpha)/M$ where $\bar{\rho}_\alpha$ is volume average value of the density of units M_α. The Landau free energy expansion (1) looks in Fourier representation as

$$\Delta\mathcal{F}\{[\tilde{\psi}_\alpha]\} = \sum_{n=2}^\infty \frac{1}{n!}\mathcal{F}_n\{[\tilde{\psi}_\alpha]\} \quad (6)$$

where the nth order contribution is described by expression

$$\mathcal{F}_n\{[\tilde{\psi}_\alpha]\} = \sum_{\{\alpha_i\}}\sum_{\{\mathbf{q}_i\}} \tilde{\Gamma}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1, \ldots, \mathbf{q}_n)$$
$$\times \delta_K(\mathbf{q}_1 + \ldots + \mathbf{q}_n)\prod_{i=1}^n \tilde{\psi}_{\alpha_i}(\mathbf{q}_i). \quad (7)$$

Equilibrium free energy F is obtained as the absolute minimum of functional (6), (7). This is completely characterized by vertex functions $\tilde{\Gamma}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q_1}, \ldots, \mathbf{q_n})$ equal to the corresponding variational derivatives of functional (1) with respect to the order parameters. These tensor-functions can be written down as

$$\tilde{\Gamma}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1, \ldots, \mathbf{q}_n) = \bar{\rho}^{n-1}\Big[f^{*(n)}_{\alpha_1\ldots\alpha_n}$$
$$- T\tilde{\gamma}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1, \ldots, \mathbf{q}_n)\Big] \quad (8)$$

where $\bar{\rho} = \bar{\rho}_1 + \ldots + \bar{\rho}_m = M/V$ denotes average density of all minimal structural units. Formula (8) differs from that introduced earlier [38] by numerical factor $\bar{\rho}^{n-1}$ due to the discrepancy in definition of the order parameters. Expression in the square brackets in the right-hand side of formula (8) is the difference of two terms describing SU and CB subsystems, respectively. The first of these terms is the component of tensor $f^{*(n)}$ which is equal to partial derivative of nth order of function $f^*(\{\rho_\alpha\})$ with respect to variables $\rho_{\alpha_1}, \ldots, \rho_{\alpha_n}$. Hence the contribution into the vertex function (8) from the SU subsystem can be presented in the form

$$\bar{\rho}^{n-1} f^{*(n)}_{\alpha_1\ldots\alpha_n} = T\Phi^{n-1}\frac{\partial^n}{\partial\Phi_{\alpha_1}\ldots\partial\Phi_{\alpha_n}}\left(\frac{f^*(\{\Phi_\alpha\})v}{T}\right) \quad (9)$$

appropriate for the calculations in terms of the "lattice liquid" model (3). As it follows from formulas (1), (6), (7), (8), the second term in formula (8) represents up to the factor T coefficient $\hat{\tilde{\gamma}}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1, \ldots, \mathbf{q}_n) = \bar{\rho}^{n-1}\tilde{\gamma}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1, \ldots, \mathbf{q}_n)$ in the expansion of the partial Lifshitz entropy

$$\mathcal{S}_L\{[\tilde{\psi}_\alpha]\} = \sum_{n=2}^\infty \frac{1}{n!}\mathcal{S}_n\{[\tilde{\psi}_\alpha]\}, \quad (10)$$

where nth order contribution is determined by formula

$$\mathcal{S}_n\{[\tilde{\psi}_\alpha]\} = \sum_{\{\alpha_i\}}\sum_{\{\mathbf{q}_i\}} \hat{\tilde{\gamma}}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1, \ldots, \mathbf{q}_n)\prod_{i=1}^n \tilde{\psi}_{\alpha_i}(\mathbf{q}_i). \quad (11)$$

Evidently, coefficients $\tilde{\gamma}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1, \ldots, \mathbf{q}_n)$ are controlled exclusively by chemical structure of a polymer specimen. This structure can be exhaustively characterized by specifying the complete set of chemical correlators of the specimen of interest [41,42]. Among them the simplest ones are one-point $Y^{(1)}_\alpha$ and two-point $Y^{(2)}_{\alpha\beta}(k)$ correlators. The first of them equals the probability for a randomly chosen monomeric unit to be M_α, whereas the second one is equal to the joint probability that a pair of randomly chosen units, separated in a macromolecule by an arbitrary sequence of k units, will be M_α and M_β. As for n-point chemical correlator $Y^{(n)}_{\alpha_1\ldots\alpha_n}(j_1, \ldots, j_{n-1})$, this represents the joint probability to find $n \geq 2$ units of given types $M_{\alpha_1}, \ldots, M_{\alpha_n}$ separated along polymer chain by arbitrary

sequences comprising, respectively, $j_1, \ldots, j_{n-1}$ units. Of prime importance in thermodynamics of heteropolymer systems are generating functions of n-point chemical correlators (gfCCs-n)

$$W_{\alpha_1\ldots\alpha_n}^{(n)}(x_1, \ldots, x_{n-1}) =$$
$$\sum_{j_1=0}^{\infty} \cdots \sum_{j_{n-1}=0}^{\infty} Y_{\alpha_1\ldots\alpha_n}^{(n)}(j_1, \ldots, j_{n-1}) \prod_{i=1}^{n-1} x_i^{j_i+1} \quad (12)$$

which specify the coefficients of the Lifshitz entropy expansion (11) [38]. In order to derive relationships expressing these coefficients through gfCCs one should solve two problems. The first of them consists in finding dependencies connecting the Fourier transforms $\tilde{\gamma}^{(n)}$ of tensor $\gamma^{(n)}$ components and correlation functions of the density fluctuations of structural units. The second problem is to express the Fourier transforms of these physical correlators through gfCCs (12). A diagram technique will be introduced below enabling the realization in practice of the earlier formulated [38] general algorithm of the solution of these two problems for melts and solutions of linear heteropolymers of arbitrary chemical structure. The solution of the above problems implies, among other things, the necessity to specify a conformational model of a polymer chain. Below we will proceed from the simplest of such models in which the vectors of all chemical bonds between monomeric units are taken to be statistically independent and to have the same length a. In this freely joint model the probability of any conformation, representing a sequence of vectors of all bonds of a polymer molecule, equals the product of the probabilities of these independent vectors. Fourier-transform $\tilde{\lambda}(\mathbf{q})$ of the distribution $\lambda(\mathbf{r})$ of random vector $\mathbf{r}$ of length $|\mathbf{r}| = a$ as well as its asymptotics at $qa \ll 1$

$$\tilde{\lambda}(\mathbf{q}) = \frac{\sin(\mathbf{q}a)}{\mathbf{q}a} \approx 1 - \frac{\mathbf{q}^2 a^2}{6} \approx \exp(-\mathbf{q}^2 a^2/6) \quad (13)$$

enter into expressions for the coefficients of the Lifshitz entropy expansion (11).

3 Vertex functions expressed through physical correlators

Since the first item in formula (8) for these functions defined by expression (9) is presumed to be known, to find them one should determine only the components of tensors $\tilde{\gamma}^{(n)}$ with different values of index n. This problem calls for several steps solution. The first of them implies the derivation of the expressions for $\hat{\tilde{\gamma}}_{\alpha_1\ldots\alpha_n}^{(n)}(\mathbf{q}_1, \ldots, \mathbf{q}_n)$ through Fourier transforms $\tilde{g}_{\alpha_1\ldots\alpha_n}^{(n)}(\mathbf{q}_1, \ldots, \mathbf{q}_n)$ of irreducible correlators $g_{\alpha_1\ldots\alpha_n}^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n)$ of the monomeric units' densities of a polymer specimen which are coeffi-

cients of functional series

$$\frac{\mathcal{F}_{CB}\{[h_\alpha]\}}{T} = \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n!} \sum_{\{\alpha_i\}} \int d\mathbf{r}_1 \ldots d\mathbf{r}_n$$
$$\times g_{\alpha_1\ldots\alpha_n}^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n) \prod_{i=1}^{n} h_{\alpha_i}(\mathbf{r}_i) \quad (14)$$

Performing the Legendre transformation (4), (5), which enables functions $\hat{\tilde{\gamma}}_{\alpha_1\ldots\alpha_n}^{(n)}(\mathbf{q}_1, \ldots, \mathbf{q}_n)$ to be expressed through $\tilde{g}_{\alpha_1\ldots\alpha_n}^{(n)}(\mathbf{q}_1, \ldots, \mathbf{q}_n)$, is a standard procedure for the Landau theory of magnetics and low-molecular weight liquids [35,36].

The second step of the solution of the above problem consists in expressing in CB subsystem the Fourier transforms of irreducible correlators through the Forurier transforms of reducible ones. This procedure for polydisperse polymers differs qualitatively from that realized in the traditional Landau theory [10]. Fundamental distinction resides here in the necessity to carry our the averaging procedure of corresponding statistical characteristics of polydisperse polymer liquid over configurations C constituting its macromolecules. Of prime importance among such characteristics are irreducible correlators resulting from configurational averaging of analogous correlators $g_{\alpha_1\ldots\alpha_n}^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n; C)$ of individual molecules. These latter can be expressed through reducible correlators

$$K_{\alpha_1\ldots\alpha_n}^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n; C) = \overline{\prod_{i=1}^{n} \rho_{\alpha_i}^m(\mathbf{r}_i; C)} \quad (15)$$

where $\rho_{\alpha_i}^m(\mathbf{r}_i; C)$ stands for the microscopic density at point $\mathbf{r}_i$ of α_i-th type units in a macromolecule with configuration C. The averaging in the right-hand part of expression (15) is accomplished over connformations of this macromolecule, i.e. over the heat disorder [40]. Reducible correlators (15) are coefficients of the expansion of partition function $Z(\{[h_\alpha]\}; C)$ of the individual molecule in powers of external fields

$$Z(\{[h_\alpha]\}; C) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \sum_{\{\alpha_i\}} \int d\mathbf{r}_1 \ldots d\mathbf{r}_n$$
$$\times K_{\alpha_1\ldots\alpha_n}^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n; C) \prod_{i=1}^{n} h_{\alpha_i}(\mathbf{r}_i) \quad (16)$$

whereas irreducible correlators $g_{\alpha_1\ldots\alpha_n}^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n; C)$ represent coefficients of an analogous expansion of the partial free energy of this molecule

$$\mathcal{F}_{CB}(\{[h_\alpha]\}; C) = -\frac{T}{M} \ln Z(\{[h_\alpha]\}; C). \quad (17)$$

Upon taking nth order variational derivatives with respect to external fields from both parts of this equality and subsequently putting these fields equal to zero it is easy to express n-point correlators $g_{\alpha_1\ldots\alpha_n}^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n; C)$ through s-point correlators $K_{\alpha_1\ldots\alpha_s}^{(s)}(\mathbf{r}_1, \ldots, \mathbf{r}_s; C)$ with $s \leq n$. When

performing configurational averaging of irreducible correlators of individual molecules, it should be borne in mind that macromolecules in a CB subsystem do not interact. As a result, the free energy of this subsystem is represented by the sum of free energies of individual molecules [29]

$$M\mathcal{F}_{CB}\{[h_\alpha]\} = \sum_C \Pi(C)\mathcal{F}_{CB}(\{[h_\alpha]\}; C)$$
$$= \Pi \langle \mathcal{F}_{CB}(\{[h_\alpha]\}; C)\rangle. \qquad (18)$$

Hereinafter angular brackets denote averaging over probability measure of configurations C where $\Pi(C)$ and Π stand, respectively, for the number of molecules of configuration C and overall number of all molecules. Expression (18) may be conveniently presented as

$$\mathcal{F}_{CB}\{[h_\alpha]\} = \frac{1}{l_{av}} \langle \mathcal{F}_{CB}(\{[h_\alpha]\}; C)\rangle \qquad (19)$$

where $l_{av} = M/\Pi$ is the average number of units in one molecule. According to expression (19) the irreducible correlator of units' densities is defined by relationship

$$g^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{r}_1,\ldots,\mathbf{r}_n) = \frac{1}{l_{av}} \left\langle g^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{r}_1,\ldots,\mathbf{r}_n; C)\right\rangle. \quad (20)$$

The above reasoning about the correlation functions of monomeric units' densities remains true for their Fourier transforms. In an momentum representation these latter will be coefficients of the expansion of the free energy and the partition function in powers of variables $\{\tilde{h}_\alpha(\mathbf{q})\}$ that are Fourier transforms of external fields $\{h_\alpha(\mathbf{r})\}$.

Let us point out some peculiarities of the Landau theory when it is formulated in momentum representation. Firstly, due to translational invariance of the system in hand among n arguments of tensor-function $\tilde{K}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n; C)$ only $n-1$ will be independent ones because the sum of all momenta is always zero. This can be mathematically formalized by means of the Kronecker delta symbol $\delta_K(\mathbf{q}_1 + \ldots + \mathbf{q}_n)$.

An important peculiarity of the Fourier transform of an arbitrary irreducible correlator $\tilde{g}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n; C)$ is its vanishing provided at least one of its arguments equals zero. That is why the expansion of functional (17) in powers of external fields $\{\tilde{h}_\alpha(\mathbf{q})\}$ comprises just those items among the arguments of which none is zeroth momentum. Hence, relationships by virtue of which the Fourier transforms of irreducible correlators $\tilde{g}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n; C)$ are expressed through the Fourier transforms of reducible ones $\tilde{K}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n; C)$ do not contain items having one-point correlators as factors

$$\tilde{g}^{(1)}_\alpha(\mathbf{q}; C) \equiv \tilde{K}^{(1)}_\alpha(\mathbf{q}; C) = \bar{l}_\alpha(C)\delta_K(\mathbf{q}) \qquad (21)$$

Each of these latter vanishing at $\mathbf{q} \neq 0$ is equal to the number $\bar{l}_\alpha(C)$ of units M_α in a macromolecule of configuration C at $\mathbf{q} = 0$.

In momentum representation two- and three-point cumulants coincide with corresponding statistical momenta

while four-point cumulant looks as follows

$$\tilde{g}^{(4)}_{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4; C) = \tilde{K}^{(4)}_{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4; C)$$
$$- \tilde{K}^{(2)}_{\alpha_1\alpha_2}(\mathbf{q}_1,\mathbf{q}_2; C)\tilde{K}^{(2)}_{\alpha_3\alpha_4}(\mathbf{q}_3,\mathbf{q}_4; C)$$
$$- \tilde{K}^{(2)}_{\alpha_1\alpha_3}(\mathbf{q}_1,\mathbf{q}_3; C)\tilde{K}^{(2)}_{\alpha_2\alpha_4}(\mathbf{q}_2,\mathbf{q}_4; C)$$
$$- \tilde{K}^{(2)}_{\alpha_1\alpha_4}(\mathbf{q}_1,\mathbf{q}_4; C)\tilde{K}^{(2)}_{\alpha_2\alpha_3}(\mathbf{q}_2,\mathbf{q}_3; C). \quad (22)$$

In general, the Fourier transform of an irreducible n-point correlator of any individual molecule is written down as an expression representing an algebraic sum of several items. Each of them has the appearance of the product of Fourier transforms of several reducible correlators, the overal number of points in which is n. Configurational averaging of both parts of this expression permits obtaining formulas for tensor-functions $\tilde{g}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n)$. Each of them at $n \geq 4$ represents the linear form of Fourier transforms of averaged reducible correlators of individual molecules

$$X^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n) = \frac{1}{l_{av}} \left\langle \tilde{K}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n; C)\right\rangle \qquad (23)$$

and various products of such correlators

$$X^{(n)}_J\left(\mathbf{q}_1^{(1)},\ldots,\mathbf{q}_{m_1}^{(1)}|\ldots|\mathbf{q}_1^{(\omega)},\ldots,\mathbf{q}_{m_\omega}^{(\omega)}\right) =$$
$$\frac{1}{l_{av}} \left\langle \prod_{\nu=1}^\omega \tilde{K}^{(m_\nu)}_{\alpha_1^{(\nu)}\ldots\alpha_{m_\nu}^{(\nu)}}\left(\mathbf{q}_1^{(\nu)}\ldots\mathbf{q}_{m_\nu}^{(\nu)}; C\right)\right\rangle. \quad (24)$$

Expression (24) corresponds to partition $J = \alpha_1^{(1)}\ldots\alpha_{m_1}^{(1)}|\ldots|\alpha_1^{(\omega)}\ldots\alpha_{m_\omega}^{(\omega)}$ into ω groups of a set of n points, each being characterized by the values of index α_i and momentum $\mathbf{q}_i$. The number of points m_ν in each ν-th group is more or equal to two [43]. For $n = 4$, for instance, there are only three different partitions J of four points into two groups containing two points each. These partitions correspond to three last items in the right-hand part of expression (22) which being averaged over configurations reads

$$\tilde{g}^{(4)}_{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4) = X^{(4)}_{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)$$
$$- X^{(4)}_{\alpha_1\alpha_2|\alpha_3\alpha_4}(\mathbf{q}_1,\mathbf{q}_2|\mathbf{q}_3,\mathbf{q}_4) - X^{(4)}_{\alpha_1\alpha_3|\alpha_2\alpha_4}(\mathbf{q}_1,\mathbf{q}_3|\mathbf{q}_2,\mathbf{q}_4)$$
$$- X^{(4)}_{\alpha_1\alpha_4|\alpha_2\alpha_3}(\mathbf{q}_1,\mathbf{q}_4|\mathbf{q}_2,\mathbf{q}_3). \quad (25)$$

In case of an arbitrary number n of points tensor-function $\tilde{g}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n)$ equals the algebraic sum of the Fourier transforms of regular (23) and "replica" (24) correlators corresponding to all possible partitions J of these points into groups comprising not less than two points.

As it follows from formula (24) the replica correlator is obtained by averaging the product of ω reducible correlator of densities of units belonging to the same polymer molecule, i.e. by averaging the product of ω correlators of its replicas. If polymer is monodisperse each replica

correlator becomes equal to the product of regular correlators (23). In case of polydisperse specimen such factorization does not take place. Hence the calculation of vertex functions implies the necessity of finding tensor-functions (24) by averaging over configurations C of the product of correlators of different replicas of an individual molecule.

The above outlined general procedure for expressing the coefficient of series (11) through correlators (23) and (24) will be exemplified by the fourth order CB subsystem vertex function related to cumulants in a following way

$$
\hat{\tilde{\gamma}}^{(4)}_{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4) = \sum_{\{\beta_i\}}\Bigg\{\tilde{g}^{(4)}_{\beta_1\beta_2\beta_3\beta_4}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)
$$
$$
- \sum_{\mathbf{p}_1\mathbf{p}_2}{}'\sum_{\mu\nu}\Big[\tilde{g}^{(3)}_{\beta_1\beta_2\mu}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{p}_1)\tilde{g}^{-1}_{\mu\nu}(\mathbf{p}_1,\mathbf{p}_2)\tilde{g}^{(3)}_{\beta_3\beta_4\nu}
$$
$$
\times(\mathbf{q}_3,\mathbf{q}_4,\mathbf{p}_2)+(2\leftrightarrow 3)+(2\leftrightarrow 4)\Big]\Bigg\}\Bigg(\prod_{i=1}^{4}\tilde{g}^{-1}_{\beta_i\alpha_i}(\mathbf{q}_i,-\mathbf{q}_i)\Bigg). \tag{26}
$$

Here two last items in square brackets are obtained by simultaneous permutations of indices and momenta of the specified points. The prime at the sum on internal momenta means that the summation does not include zero value of a momentum. Going in formula (26) from Fourier transforms of cumulants (20) to correlators (23), (24) we will arrive at the known expression [29]

$$
\hat{\tilde{\gamma}}^{(4)}_{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4) = \hat{\tilde{\gamma}}^{(4),reg}_{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)
$$
$$
+ \hat{\tilde{\gamma}}^{(4),nloc}_{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4) \tag{27}
$$

where regular and nonlocal contributions to the vertex function of the CB subsystem are presented by expressions [44]

$$
\hat{\tilde{\gamma}}^{(4),reg}_{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4) = \sum_{\{\beta_i\}}\Bigg(\prod_{i=1}^{4}X^{-1}_{\alpha_i\beta_i}(\mathbf{q}_i)\Bigg)
$$
$$
\times\Bigg\{X^{(4)}_{\beta_1\beta_2\beta_3\beta_4}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4) - \sum_{\mathbf{p}}\sum_{\mu\nu}\Big[X^{(3)}_{\beta_1\beta_2\mu}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{p})
$$
$$
\times X^{-1}_{\mu\nu}(\mathbf{p})X^{(3)}_{\beta_3\beta_4\nu}(\mathbf{q}_3,\mathbf{q}_4,-\mathbf{p}) + (2\leftrightarrow 3) + (2\leftrightarrow 4)\Big]\Bigg\} \tag{28}
$$

$$
\hat{\tilde{\gamma}}^{(4),nloc}_{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4) = \sum_{\{\beta_i\}}\Bigg(\prod_{i=1}^{4}X^{-1}_{\alpha_i\beta_i}(\mathbf{q}_i)\Bigg)
$$
$$
\times\Bigg\{\Big[X^{(4)}_{\beta_1\beta_2|\beta_3\beta_4}(\mathbf{q}_1,\mathbf{q}_2|\mathbf{q}_3,\mathbf{q}_4) - \sum_{\mu\nu}X^{(3)}_{\beta_1\beta_2\mu}(\mathbf{q}_1,\mathbf{q}_2,0)
$$
$$
\times X^{-1}_{\mu\nu}(0)X^{(3)}_{\beta_3\beta_4\nu}(\mathbf{q}_3,\mathbf{q}_4,0)\Big] + \Big[(2\leftrightarrow 3)\Big] + \Big[(2\leftrightarrow 4)\Big]\Bigg\}. \tag{29}
$$

The presence of the nonlocal contribution to vertex functions is the most important peculiarity inherent to the Landau theory of polydisperse polymers highlighted for the first time in papers [25,28,27]. This contribution involves positive and negative parts. The first of them is due to averaging of the product of the correlators of monomeric units' densities over configurations of individual molecules whereas the second part is related to the extension of the summation over internal momenta to their zeroth value.

In the Landau theory of monodisperse polymer liquids both parts of the nonlocal contribution mutually annihilate. This can be readily noticed when considering four-point vertex functions described by formula (29). So, in the absence of polydispersity the replica correlator in this formula admits factorization into the product of the couple of two-point correlators. The sum appearing in square brackets is reduced just to the same expression. It can be shown using relationships

$$
X^{(3)}_{\alpha_1\alpha_2\alpha_3}(\mathbf{q},-\mathbf{q},0) = X_{\alpha_1\alpha_2}(\mathbf{q},-\mathbf{q})X_{\alpha_3}(0),
$$
$$
\lim_{\mathbf{p}\to 0}\sum_{\alpha_1\alpha_2}X_{\alpha_1}(0)X_{\alpha_2}(0)X^{-1}_{\alpha_1\alpha_2}(\mathbf{p},-\mathbf{p}) = 1 \tag{30}
$$

valid for any monodisperse polymers.

Under the description of polydisperse polymer liquids in terms of the Landau theory each vertex function, starting with the four-point one, can be presented as a sum of regular and nonlocal contributions. In the next section a diagram technique will be introduced enabling one to express in a simple way these contributions through physical correlators (23) and (24) for the vertex function with arbitrary number n of points.

4 Diagram technique

This technique is developed to construct a rather simple algorithm that permits formulating in diagram language a procedure providing the possibility to immediately write down an expression for the contribution of any nth order into the Lifshitz entropy (11). To this end it is necessary to specify the complete set of the diagram technique elements and to formulate the rules of their composition. Such a set pictured in Figure 1 comprises an open circle, lines and regular n-gons. Each vertex of these latter is supplied with label $\zeta = (\alpha,\mathbf{q})$ characterized by values of index α and momentum $\mathbf{q}$. Identical labels are ascribed to other diagram elements in Figure 1. To them there correspond the following analytical expressions:

1) Open circle is the Fourier transform of the parameter of order $\tilde{\psi}_\alpha(\mathbf{q})$.

2) Solid line represents the element of the matrix inverse to that with elements

$$
X^{(2)}_{\alpha_1\alpha_2}(\mathbf{q}_1,\mathbf{q}_2) \equiv X_{\alpha_1\alpha_2}(\mathbf{q}_1,\mathbf{q}_2)
$$
$$
\equiv X_{\alpha_1\alpha_2}(\mathbf{q}_1)\delta_K(\mathbf{q}_1+\mathbf{q}_2). \tag{31}
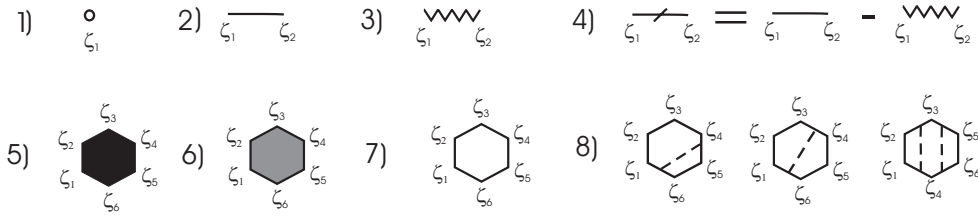$$

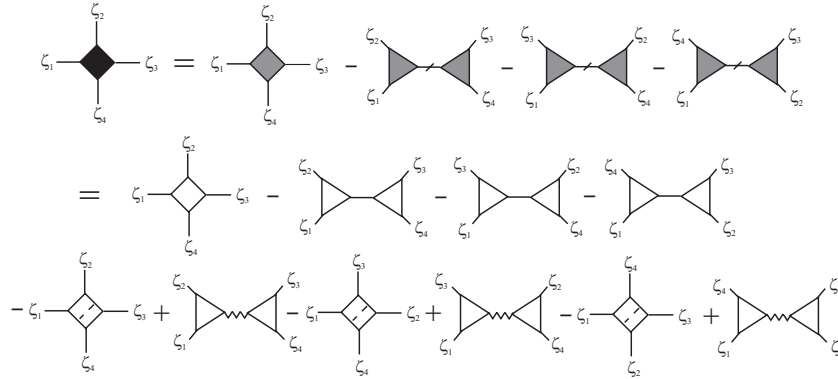**Fig. 1.** Elements of the diagram technique.

Fig. 2. The fourth vertex $\hat{\tilde{\gamma}}^{(4)}$.

3) Zigzag line corresponds to element $X_{\alpha_1\alpha_2}^{(-1)}$ of matrix inverse to that with elements $X_{\alpha_1\alpha_2} = X_{\alpha_1\alpha_2}(0)$.

4) Crossed line is the element of matrix equal to the difference of matrices with elements $X_{\alpha_1\alpha_2}^{-1}(\mathbf{q}_1)\delta_K(\mathbf{q}_1+\mathbf{q}_2)$ and $X_{\alpha_1\alpha_2}^{-1}$.

5) Black n-gon depicts the components of a tensor whose convolution with matrix elements $X_{\alpha_i\alpha_j}^{-1}(\mathbf{q}_i, \mathbf{q}_j)$ yields the tensor with components $\hat{\tilde{\gamma}}_{\alpha_1\ldots\alpha_n}^{(n)}(\mathbf{q}_1,\ldots,\mathbf{q}_n)$. Henceforward, unless otherwise stated, the term convolution means not only summing over indices but integrating (*summing*) over momenta as well.

6) Gray n-gon is the Fourier transform of irreducible correlation function $\tilde{g}_{\alpha_1\ldots\alpha_n}^{(n)}(\mathbf{q}_1,\ldots,\mathbf{q}_n)$ (20).

7) White n-gon is the *regular* averaged reducible correlator (23). The sum of momenta of all n apices is equal to zero.

8) White n-gon partitioned by dotted lines into ω parts, each ν-th of which contains $m_\nu \geq 2$ apices, corresponds to the *replica* averaged reducible correlator (24). The sum of momenta of apices inside each ν-th group equals zero.

Among all polygons depicted in Figure 1 only one, with $n = 6$ apices, is chosen as an illustration. For such a hexagon there are three possible types of the apices' partition into groups. Examples of partitions of each of these three types are shown in diagram 8 of Figure 1.

Diagram elements serve as "bricks", linking which one can draw pictures equivalent to the analytical expressions presented in the preceding sections. An apex of a polygon can be joined to one of the line ends only if the labels of the elements to be joined coincide. Let us call the lines,

$$S_L\{[\widetilde{\psi_\alpha}]\} = -\frac{1}{2!} \text{○─○} + \frac{1}{3!} \triangle + \frac{1}{4!} \text{◇} + \frac{1}{5!} \pentagon$$

$$+ \frac{1}{6!} \hexagon + \cdots$$

Fig. 3. Diagrammatic representation of contributions to the Lifshitz entropy.

both ends of which are joined to polygons, internal edges to distinguish them from external ones, attached exclusively to one polygon. The second end of these latter can either be linked to the open circle or be unlinked. The summation is performed here over all conjunction points while labels are retained only for free ends of lines if these are present on diagrams. To exemplify the above reasoning we adduced in Figure 2 graphical representation of function $\hat{\tilde{\gamma}}_{\alpha_1\alpha_2\alpha_3\alpha_4}^{(4)}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4)$. Diagrams in the first row of this figure correspond to expression (26) whereas the second and the third rows represent a pictorial form of analytical expressions, respectively, for regular (28) and nonlocal (29) parts of the Fourier transform of four-point vertex function in CB subsystem.

Once the diagram elements have been introduced we come to the construction on their basis of the contributions (11) into the partial Lifshitz entropy whose expansion (10) is demonstrated in Figure 3. In consonance with the above outlined analytical procedure of the determination of these contributions, first, it is necessary to express black polygons through gray ones to subsequently
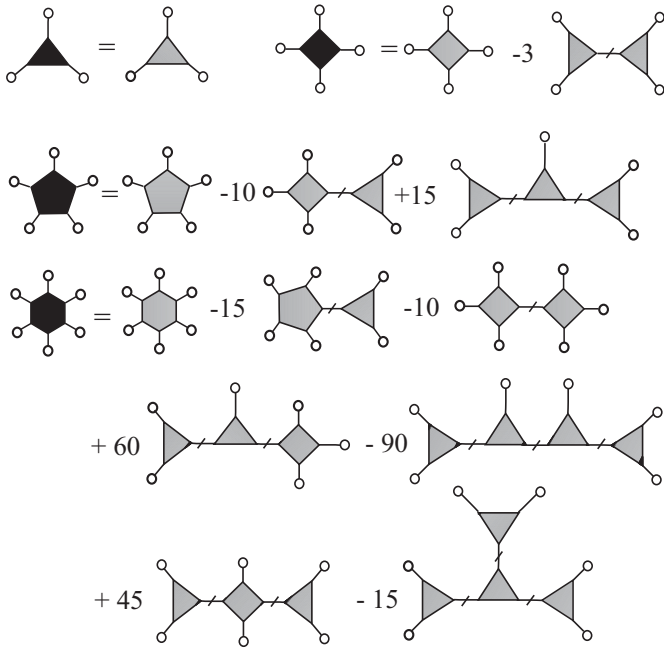
Fig. 4. The vertex functions $\hat{\tilde{\gamma}}^{(n)}$, $(n = 3, 4, 5, 6)$ expressed via irreducible correlators.

"substitute" them into diagrams of Figure 3. This procedure leads to the diagram expressions some of which are depicted in Figure 4 [38]. To obtain them the following algorithm was employed.

In order to determine nth order contribution first of all one should draw all possible tree-like diagrams, each containing n external edges which link apices of gray polygons with pending vertices. Solid lines correspond to these external edges unlike crossed lines corresponding to internal ones. Deletion of any of such p edges in a tree-like diagram results in its splitting into two diagrams. A diagram can enter into the expression for $\mathcal{S}_n\{[\tilde{\psi}_\alpha]\}$ (11) with any sign equal to $(-1)^p$. The numerical coefficient in front of a diagram (see Fig. 4) composed of n gray polygons, every ith of which has n_i external edges, can be determined by formula $n!/[(n_1!n_2!\ldots)\varsigma]$. To find coefficient ς it is necessary to switch from the diagram of interest to its graph by replacing each gray k-gon by corresponding node. Then coefficient ς will be equal to the order of the group of automorphisms of the mentioned graph.

The next stage of the development of the diagram technique suggests the formulation of a graphical algorithm for the construction of diagrams corresponding to regular and nonlocal contributions into the partial Lifshitz entropy. The first of them is rather easy to find. Hence the regular nth order contribution is obtained from corresponding diagrams, identical to those presented in Figure 4, by replacing all gray polygons in them by white polygons and crossed lines by noncrossed ones. This operation leads to the diagrams previously presented in review [38].

To find the nonlocal contribution recourse should be made to the two- step procedure which is an extension of that employed for the derivation of expression (27). This procedure is realized as follows:

1) At the first step the crossed lines (Fig. 1, (4)) linking in diagrams gray polygons should be changed for the solid noncrossed (Fig. 1, (2)) and zigzag (Fig. 1, (3)) lines. In the course of this procedure the diagrams with zeroth external momentum should be discarded since their contribution to the free energy is equal to zero.

2) At the second step it is necessary to present every gray polygon as an algebraic sum of diagrams each of which with an accuracy of the prefactor is white polygon cut by $\omega - 1$ dotted line into ω parts. Such a diagram corresponds to the certain partition of marked apices of gray n-gon into groups, each containing not less than two representatives. The above apex can be either internal or external depending on the type of the adjacent edge. Each ν-th group is characterized by a pair of integers $(m_\nu^{(in)}, m_\nu^{(ex)})$ indicating how many internal and external apices it contains. Specification of such pairs for all ω groups of a certain partition completely characterizes the type $\pi = \{(m_\nu^{(in)}, m_\nu^{(ex)})\}$ of this partition of the polygon in hand. So, 5-gon having $n^{(in)} = 1$ internal apex and $n^{(ex)} = 4$ external apices admits just two types of different partitions, $\pi_1 = \{(0, 2)(1, 2)\}$ and $\pi_2 = \{(0, 3)(1, 1)\}$. Any marked diagram comprising f gray labeled polygons is presented as the sum of all its possible partitions, each being specified by the set of particular partitions of the polygons involved. Type Ω of the partition of the above diagram is fully prescribed by types $\pi^{(1)}, \ldots, \pi^{(f)}$ of these polygons' partitions. Evidently, all labeled diagrams of the same type Ω will yield after the convolution with the components of the parameter of order the identical contribution to the Lifshitz entropy. Due to the mutual independence of the partitions of polygons of any type Ω gray diagram its prefactor will equal the product of the prefactors of all white nonlabeled polygons presented in this diagram

$$D(\Omega) = \prod_{j=1}^{f} D\left(\pi^{(j)}\right). \tag{32}$$

As for prefactor $D(\pi)$ of such a polygon, corresponding to its particular partition $\pi = \{(m_\nu^{(in)}, m_\nu^{(ex)})\}$, this can be calculated by formula

$$D(\pi) = \frac{(-1)^{\omega-1}}{\omega} \sum_{\{a_\nu\}} \sum_{\{b_\nu\}} \frac{n^{(in)}!}{a_1!\ldots a_\omega!} \frac{n^{(ex)}!}{b_1!\ldots b_\omega!}$$
$$\times \delta_K \left(n^{(in)} - \sum_{\nu=1}^{\omega} a_\nu\right) \delta_K \left(n^{(ex)} - \sum_{\nu=1}^{\omega} b_\nu\right)$$
$$\times \prod_{\nu=1}^{\omega} \delta_K \left(m_\nu - a_\nu - b_\nu\right). \tag{33}$$

Here summing is performed over all possible sets of indices $(a_1, \ldots, a_\omega)$ and $(b_1, \ldots, b_\omega)$, provided indices a_ν and b_ν at any $\nu = 1, \ldots, \omega$ run, respectively, values $\{m_1^{(in)}, m_2^{(in)}, \ldots, m_\omega^{(in)}\}$ and $\{m_1^{(ex)}, m_2^{(ex)}, \ldots, m_\omega^{(ex)}\}$. The factor in front of double sum in expression (32) results from the logarithm expansion whereas this very sum
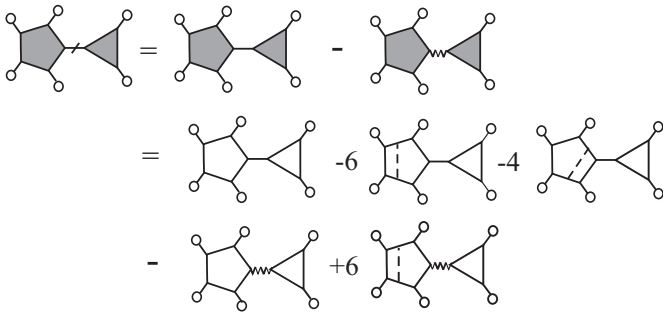
Fig. 5. The diagrammatic separation of the regular and non-local terms.

Fig. 6. The non-local part of fourth vertex.

represents the solution of a certain combinatoric problem. The latter may be formulated if to the polygons' internal and external vertices black and white balls are put in correspondence, respectively. Then double sum in formula (32) will coincide with the number of ways in which the set of balls, consisting of $n^{(in)}$ indistinguishable black and $n^{(ex)}$ indistinguishable white balls can be partitioned among ω different urns in such a manner that one urn will contain $(m_1^{(in)}, m_1^{(ex)})$ balls of corresponding colors, other urn will contain $(m_2^{(in)}, m_2^{(ex)})$ balls, and so on.

When switching from gray diagrams to the white ones these latter are divided into nonoverlapping fragments whose borders are presented by dotted and zigzag lines. A fragment can comprise pending vertices attached to different polygons. Essentially, the sum of all momenta entering in any of the mentioned fragments is equal to zero. This means that calculating the contribution from some white diagram into the Lifshitz partial entropy one should take into account the presence in the integrand of the product of the Kronecker delta symbols, each having as argument overall momentum of all pending vertices present in the corresponding diagram fragment.

Figure 5 demonstrates the example of switching from gray diagrams to white ones in accordance with the above formulated two-step procedure. The diagram presented in this figure contains two gray polygons, having $(n_1^{(in)} = 1, n_1^{(ex)} = 4)$ and $(n_2^{(in)} = 1, n_2^{(ex)} = 2)$, respectively. The only type of the partition $(1,2)$ which the triangle admits is the trivial one $\omega = 1$, whereas the pentagon allows along with the trivial type of the partition $(1,4)$ also two non-trivial ones with $\omega = 2$, one of them being $(0,2)$ $(1,2)$ and another – $(0,3)$ $(1,1)$. To these partition types there correspond, respectively, three white diagrams in the second row of Figure 5, whose prefactors found from formulas (31), (32) are equal to $1, (-6)$ and (-4). The third diagram in the third row in this figure is absent since its middle fragment comprises the pending vertex with the zeroth momentum.

The above outlined two-step procedure permits expressing any gray diagram through white ones. Because in the foregoing we have already formulated the rules for expressing black diagrams through gray ones (see, for example, Fig. 4), the problem of the construction of a general
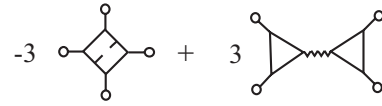
graphical algorithm enabling one to express the contribution of any order $\mathcal{S}_n\{[\tilde{\psi}_\alpha]\}$ (11) into the partial Lifshitz entropy (10) through the Fourier transforms of the reducible correlators (23), (24) may be regarded as already solved.

At values $n \geq 4$ this contribution will include two types of items, some of which describe the regular part of this contribution whereas some other characterize the nonlocal one. To the items of the first type which further will be referred to as regular ones there correspond such white diagrams that do not contain dotted and zigzag lines. To the second type items termed nonlocal ones there correspond the rest of white diagrams. Figures 6, 7, 8, 9, 10 contain diagrams for the forth-, fifth- and sixth-order nonlocal items. Diagrams depicted in Figure 6 are well known [38] whereas those in other figures are presented for the first time.

To demonstrate the canceling of nonlocal parts of contributions into the Lifshitz entropy of a polymer system in the absence of polydispersity it is possible to resort to the following speculative procedure. Each n-gon in white diagrams like those presented in Figures 6, 7, 8, 9, 10 should be cut into separate fragments along dotted and across zigzag lines. The first cut corresponding to the absence of the averaging over configurations of macromolecules permits splitting the Fourier-transforms of replica correlators entering in expressions (24). The second cut corresponding to the application of an equality of type (30) also leads to factorization of each diagram contribution. It can be easily shown that the contributions of diagrams obtained by such two cuts exactly annihilate each other. As a result the nonlocal part of any order contribution into the Lifshitz entropy will vanish.

Once completed the derivation of diagram technique which allows the compact expression of vertex functions $\hat{\tilde{\gamma}}^{(n)}$ (11) in terms of generalized correlators $X^{(n)}$ (23), (24), let us discuss the procedure designed for the expression of the generalized correlators in terms of *gfCC*s (12).

5 Expression of generalized physical correlators through gfCCs

5.1 Regular correlators

Those of them arising when the coordinates of at least two points coincide invite a special consideration. With this in mind it is convenient to switch from the Fourier transforms of correlators $X_{\alpha_1...\alpha_n}^{(n)}(\mathbf{q}_1, \ldots, \mathbf{q}_n)$ to those of correlators $\tilde{\theta}_{\alpha_1...\alpha_n}^{(n)}(\mathbf{q}_1, \ldots, \mathbf{q}_n)$ defined on the set of points whose coordinates do not coincide. To do this, in diagrams for $X^{(n)}$
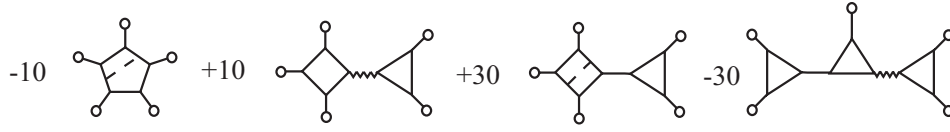
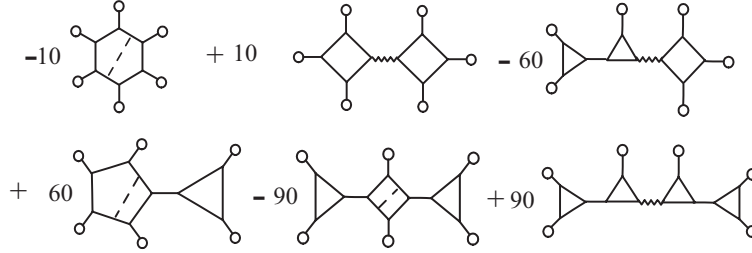**Fig. 7.** The non-local part of fifth vertex.

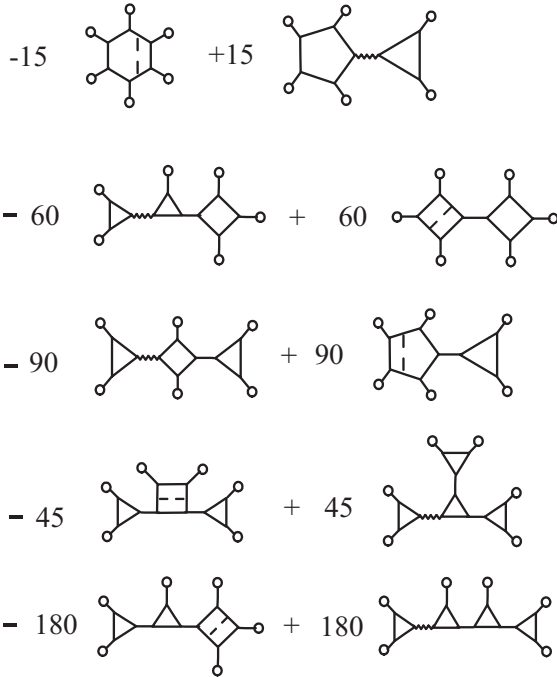**Fig. 8.** The non-local part of sixth vertex I. Each of two fragments contains three pending vertices.

Fig. 9. The non-local part of sixth vertex II. One fragment contains four pending vertices whereas another contains two ones.

expression corresponds

$$
X^{(3)}_{\alpha_1\alpha_2\alpha_3}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3) = \delta_K(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)\left\{\delta_{\alpha_1\alpha_2}\delta_{\alpha_2\alpha_3}\theta_{\alpha_1}\right.
$$
$$
+ \delta_{\alpha_1\alpha_2}\tilde{\theta}^{(2)}_{\alpha_1\alpha_3}(\mathbf{q}_1+\mathbf{q}_2,\mathbf{q}_3) + \delta_{\alpha_2\alpha_3}\tilde{\theta}^{(2)}_{\alpha_1\alpha_2}(\mathbf{q}_1,\mathbf{q}_2+\mathbf{q}_3)
$$
$$
\left. + \delta_{\alpha_1\alpha_3}\tilde{\theta}^{(2)}_{\alpha_2\alpha_3}(\mathbf{q}_2,\mathbf{q}_1+\mathbf{q}_3) + \tilde{\theta}^{(3)}_{\alpha_1\alpha_2\alpha_3}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)\right\}. \quad (34)
$$

Concentric circles in Figure 11 can be replaced by ordinary ones provided the product of the Kroneker deltas of coincident points' indices is introduced. The algorithm allowing one to express $X^{(n)}$ of an arbitrary order via $\tilde{\theta}^{(n)}$ is quite evident.

The transition from tensor-functions $X^{(n)}$ to $\tilde{\theta}^{(n)}$ is imperative because just these latter are expressed directly through $W^{(n)}$ (12). The algorithm of the derivation of such expressions is rather simple since by virtue of function $\tilde{\theta}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n)$ symmetry with respect to any permutations n of its labels the latter is representable by the sum of $n!$ items. Each of them is obtained from the so-called "base function"

$$
W^{(n)}_{\alpha_1\alpha_2\ldots\alpha_n}(e_1,e_2,\ldots,e_{n-1}),
$$
$$
e_i = \tilde{\lambda}(\mathbf{Q}_i), \qquad \mathbf{Q}_i = \sum_{f=1}^{i}\mathbf{q}_f \quad (35)
$$

by one of $n!$ permutations of its labels. The notion of base functions is of importance in the framework of the formalism outlined in this paper. The labels' permutation operation applied to each of these functions generates a family of "principal functions". Being specified on a set of n points every such function is characterized by particular sequence of their indices and is in a certain way dependent on the momentum of these points.

The arguments of base function (35) can be found using a simple graphical algorithm, whose rigorous substantiation is presented in Appendix A. For this purpose one
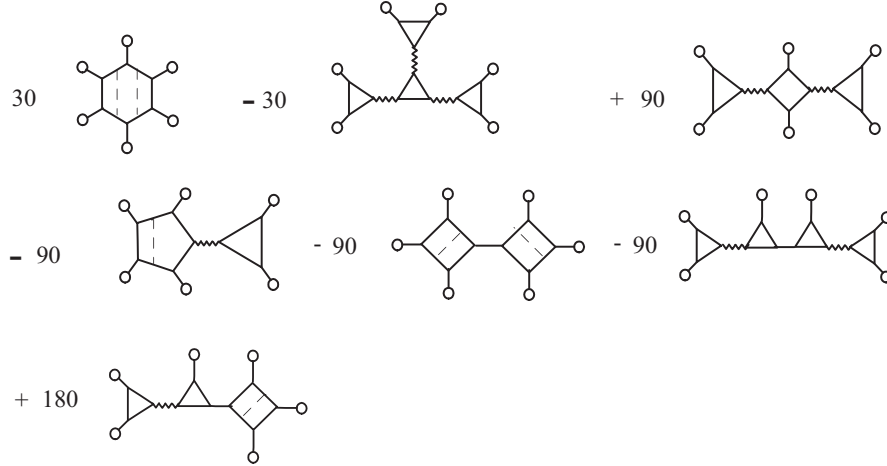
an additional type of apex should be introduced resulting from the contraction in one of several initial apices. An apex formed by such a contraction is labeled by any of indices and total momentum of contracted apices. For each tensor-function $X^{(n)}$ there are different fashions of apices' contraction in its diagram. These correspond to different partitions of the set of apices into subsets with identical apices' indices. Function $X^{(n)}$ is the sum of contributions from all possible partitions. For example, to the diagram representation of $X^{(3)}$ depicted in Figure 11 the analytical

Fig. 10. The non-local part of sixth vertex III. Each of three fragments contains two pending vertices.
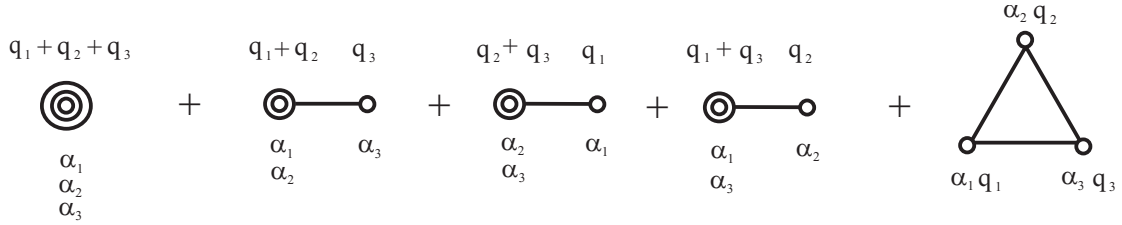

Fig. 11. Diagrammatic representation of $X^{(3)}_{\alpha_1\alpha_2\alpha_3}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)$.

should place n points on a straight line and having ascribed a label to each point to link the neighboring points by arches. The weight of an arch linking points α_i and α_{i+1} is taken to be equal to e_i.

The above mentioned symmetry property of tensor-function $\tilde{\theta}^{(n)}$ allows, in some instances, to substantially simplify expressions for the contributions into the free energy. The fact is that to find these expressions the necessity arises to perform the operation of tensor-functions $\tilde{\theta}^{(n)}$ contraction, generally speaking, both with function

$$z_\alpha(\mathbf{q}) = \sum_\beta \left[X^{-1}(\mathbf{q})\right]_{\alpha\beta} \tilde{\psi}_\beta(\mathbf{q}) \qquad (36)$$

and with matrix-functions X^{-1} (31). Due to the above symmetry some of $n!$ items obtained by the contraction of principal functions can turn out to be identical. Such a situation takes place if these principal functions differ solely by permutations of the labels whereby their contraction with functions (31) is performed. Thus, all $n!$ items are divided into r groups, in each of which they are identical. Consequently when calculating the free energy it suffices to find just one of the items in each group and multiply it by the number of its elements. Hence to carry out function $\tilde{\theta}^{(n)}$ contraction with several functions (36) the knowledge is needed of rm^n independent principal functions.

Let us illustrate the above general statement for $n = 3$ when the following expression holds

$$\tilde{\theta}^{(3)}_{\alpha_1\alpha_2\alpha_3}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) = W^{(3)}_{\alpha_1\alpha_2\alpha_3}(b_1, b_3) + W^{(3)}_{\alpha_2\alpha_1\alpha_3}(b_2, b_3)$$

$$+ W^{(3)}_{\alpha_1\alpha_3\alpha_2}(b_1, b_2) + W^{(3)}_{\alpha_2\alpha_3\alpha_1}(b_2, b_1)$$

$$+ W^{(3)}_{\alpha_3\alpha_1\alpha_2}(b_3, b_2) + W^{(3)}_{\alpha_3\alpha_2\alpha_1}(b_3, b_1)$$

$$b_i = \tilde{\lambda}(\mathbf{q}_i), \quad (i = 1, 2, 3). \qquad (37)$$

In finding the contribution to the free energy from the third order vertex a term arises wherein $\tilde{\theta}^{(3)}$ contracts with three functions (36). Here $r = 1$ and thus

$$\sum_{\{\alpha\}} \sum_{\{\mathbf{q}\}} \tilde{\theta}^{(3)}_{\alpha_1\alpha_2\alpha_3}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) z_{\alpha_1}(\mathbf{q}_1) z_{\alpha_2}(\mathbf{q}_2) z_{\alpha_3}(\mathbf{q}_3)$$

$$\times \, \delta_K(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3)$$

$$= 6 \sum_{\{\alpha\}} \sum_{\{\mathbf{q}\}} W^{(3)}_{\alpha_1\alpha_2\alpha_3}(e_1, e_2) z_{\alpha_1}(\mathbf{q}_1) z_{\alpha_2}(\mathbf{q}_2) z_{\alpha_3}(\mathbf{q}_3)$$

$$\times \, \delta_K(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3). \qquad (38)$$

Hence to have the contribution (38) calculated, it is enough to find m^3 principal functions $W_{\alpha_1\alpha_2\alpha_3}(e_1, e_2)$.

For diagrams with internal edges at least those principal functions yield after the contraction the same contribution, which are obtained by all possible permutations of

external apices. For instance, one of the fourth-order contributions into the free energy from $\hat{\tilde{\gamma}}^{(4)(reg)}$ is simplified as follows

$$\sum \tilde{\theta}^{(3)}_{\alpha_1\alpha_2\nu}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{p}) X^{-1}_{\nu\mu}(\mathbf{p}) \tilde{\theta}^{(3)}_{\alpha_3\alpha_4\mu}(\mathbf{q}_3, \mathbf{q}_4, -\mathbf{p})$$

$$\times \delta_K(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{p}) \delta_K(\mathbf{q}_3 + \mathbf{q}_4 - \mathbf{p}) \prod_i z_{\alpha_i}(\mathbf{q}_i)$$

$$= 4 \sum \left[W^{(3)}_{\alpha_1\alpha_2\nu}(b_1, b_p) + W^{(3)}_{\alpha_1\nu\alpha_2}(b_1, b_2) + W^{(3)}_{\nu\alpha_1\alpha_2}(b_p, b_2) \right]$$

$$\times \left[W^{(3)}_{\alpha_3\alpha_4\mu}(b_3, b_p) + W^{(3)}_{\alpha_3\mu\alpha_4}(b_3, b_4) + W^{(3)}_{\mu\alpha_3\alpha_4}(b_p, b_4) \right]$$

$$\times X^{-1}_{\nu\mu}(\mathbf{p}) \delta_K(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{p}) \delta_K(\mathbf{q}_3 + \mathbf{q}_4 - \mathbf{p}) \prod_i z_{\alpha_i}(\mathbf{q}_i) \tag{39}$$

where $\sum(\ldots) = \sum_{\{\alpha_i\}} \sum_{\{\mathbf{q}_i\}} \sum_{\nu\mu} \sum_{\mathbf{p}}(\ldots)$ and b_i was defined above (37) whereas $b_p = \tilde{\lambda}(\mathbf{p})$. To comment on equality (39) let us note that this expression contains two functions $\tilde{\theta}^{(3)}$ each being contracted with two functions (36). For every function $\tilde{\theta}^{(3)}$ the number of the groups $r = 3$ having two elements each. If under the calculation of a diagram the contraction of functions $\tilde{\theta}^{(3)}$ is realized with no more than one function (36) no simplifications due to symmetry of $\tilde{\theta}^{(3)}$ occur. This is because in these cases $r = 6$, so that each group comprises a sole element.

For a symmetric copolymer (wherein the probability to find any sequence of units equals, by definition, that of a mirror reflected one) function $\tilde{\theta}^{(n)}$ depends on smaller number of principal functions. So, function $\tilde{\theta}^{(3)}$ (37) for such a copolymer reads

$$\tilde{\theta}^{(3)}_{\alpha_1\alpha_2\alpha_3}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) = 2 \left[W^{(3)}_{\alpha_1\alpha_2\alpha_3}(b_1, b_3) \right.$$

$$\left. + W^{(3)}_{\alpha_2\alpha_1\alpha_3}(b_2, b_3) + W^{(3)}_{\alpha_1\alpha_3\alpha_2}(b_1, b_2) \right]. \tag{40}$$

5.2 Replica correlators

As in the case of ordinary correlators here it is necessary to go over from tensor-functions $X^{(n)}$ to functions $\tilde{\theta}^{(n)}$ defined on the set of distinct points. The principle underlying this procedure remains unaltered. As before the point formed under the contraction of several points is assigned any of indices of these coincident points and their total momentum. For example, when the second point in the first group and the first point in the second group coincide, function $\tilde{\theta}^{(4);(2)}_{\alpha_1^{(1)}\alpha_2^{(1)}\alpha_1^{(2)}\alpha_2^{(2)}}(\mathbf{q}_1^{(1)}, \mathbf{q}_2^{(1)}, \mathbf{q}_1^{(2)}, \mathbf{q}_2^{(2)})$ transforms into function

$$\tilde{\theta}^{(3);(2)}_{\alpha_1^{(1)}\alpha_2^{(1)}\alpha_2^{(2)}}\left(\mathbf{q}_1^{(1)}, \mathbf{q}_2^{(1)} + \mathbf{q}_1^{(2)}, \mathbf{q}_2^{(2)}\right) \delta_{\alpha_2^{(1)}\alpha_1^{(2)}}. \tag{41}$$

Under fixed n-point partition $\{m_\nu\}$ the function $\tilde{\theta}^{(n);(\omega)}(\{m_\nu\})$ is written down at any ω, like in the local case, as a sum of $n!$ items, each being equal to n-point principal function. Function $\tilde{\theta}^{(n);(\omega)}(\{m_\nu\})$ is, by definition, symmetric only with respect to any permutations of the labels of the points within each group. Such a symmetry, however, is absent under the permutations of the labels of apices belonging to different groups.

In view of the mentioned symmetry among $n!$ of n-point principal functions which add up to $\tilde{\theta}^{(n);(\omega)}(\{m_\nu\})$ it will suffice to determine arguments of just $N = n!/(m_1! \ldots m_\omega!)$ base functions. Let us choose as these latter such principal functions whose indices are ordered, i.e. point $\alpha_k^{(\nu)}$ is situated to the left of the point $\alpha_{k+1}^{(\nu)}$ for any $\nu = 1, \ldots, \omega$. Arguments of other principal functions can by obtained by intragroup permutations of labels in base functions.

Arguments of base functions can be found using a simple graphical algorithm. To this end, let us put in correspondence to every group of the partition chosen a horizontal line with number of points m_ν equal to that of elements in ν-th group. The mutual arrangement of n such points on ω straight lines specifies their ordered configuration Ω, which unambiguously corresponds to a certain base function. For instance, for $n = 4$ there are 6 base functions corresponding to the following configurations

$$1) \left\{\alpha_1^{(1)}, \alpha_2^{(1)}, \alpha_1^{(2)}, \alpha_2^{(2)}\right\}, \quad 2) \left\{\alpha_1^{(1)}, \alpha_1^{(2)}, \alpha_2^{(1)}, \alpha_2^{(2)}\right\},$$

$$3) \left\{\alpha_1^{(1)}, \alpha_1^{(2)}, \alpha_2^{(2)}, \alpha_2^{(1)}\right\}, \quad 4) \left\{\alpha_1^{(2)}, \alpha_2^{(2)}, \alpha_1^{(1)}, \alpha_2^{(1)}\right\},$$

$$5) \left\{\alpha_1^{(2)}, \alpha_1^{(1)}, \alpha_2^{(2)}, \alpha_2^{(1)}\right\}, \quad 6) \left\{\alpha_1^{(2)}, \alpha_1^{(1)}, \alpha_2^{(1)}, \alpha_2^{(2)}\right\}. \tag{42}$$

Once erected a perpendicular from every point, all horizontal straight lines are divided into $(n - 1)$ intervals. Thereafter it is necessary to link the neighboring points of each group by arches. The weight of an arch in every group is defined as in the previous subsection, whereas the weight of the interval equals the product of the weights of the arches embracing this interval. Then ith argument x_i of $gfCC$ (12) will be determined by the weight of the ith interval. If no arch embraces the interval in hand its weight is put equal to unity. Given the arguments of all N base functions, the remaining $(m_1! \ldots m_\omega!)$ principal functions of the families generated by these base functions can be obtained by labels' permutations within the groups.

Due to function $\tilde{\theta}^{(n);(\omega)}$ symmetry with respect to the labels' permutations within the groups, its contraction with functions (36) leads to the appearance of only N different items, each representing the sum of $(m_1! \ldots m_\omega!)$ identical terms.
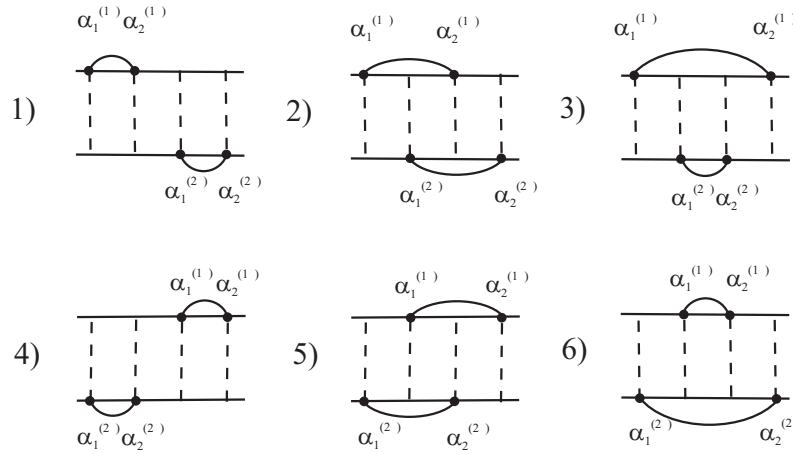
Fig. 12. Base functions $w^{(4)}$.

Inspecting Figure 12 it is easy to write down the arguments of six base functions

$$1)\ W^{(4)}_{\alpha_1^{(1)}\alpha_2^{(1)}\alpha_1^{(2)}\alpha_2^{(2)}}\left(e_1^{(1)}, 1, e_1^{(2)}\right)$$

$$2)\ W^{(4)}_{\alpha_1^{(1)}\alpha_1^{(2)}\alpha_2^{(1)}\alpha_2^{(2)}}\left(e_1^{(1)}, e_1^{(1)}e_1^{(2)}, e_1^{(2)}\right)$$

$$3)\ W^{(4)}_{\alpha_1^{(1)}\alpha_1^{(2)}\alpha_2^{(2)}\alpha_2^{(1)}}\left(e_1^{(1)}, e_1^{(1)}e_1^{(2)}, e_1^{(1)}\right)$$

$$4)\ W^{(4)}_{\alpha_1^{(2)}\alpha_2^{(2)}\alpha_1^{(1)}\alpha_2^{(1)}}\left(e_1^{(2)}, 1, e_1^{(1)}\right)$$

$$5)\ W^{(4)}_{\alpha_1^{(2)}\alpha_1^{(1)}\alpha_2^{(2)}\alpha_2^{(1)}}\left(e_1^{(2)}, e_1^{(2)}e_1^{(1)}, e_1^{(1)}\right)$$

$$6)\ W^{(4)}_{\alpha_1^{(2)}\alpha_1^{(1)}\alpha_2^{(1)}\alpha_2^{(2)}}\left(e_1^{(2)}, e_1^{(2)}e_1^{(1)}, e_1^{(2)}\right). \qquad (43)$$

Hereinafter the following designations are employed

$$e_i^{(\nu)} = \tilde{\lambda}(\mathbf{Q}_i^\nu), \quad \mathbf{Q}_i^\nu = \sum_{f=1}^i \mathbf{q}_f^{(\nu)}. \qquad (44)$$

Intragroup permutations of the labels in functions (43) permit finding all $4! = 24$ principal functions whose sum is equal to function $\tilde{\theta}_4^{(2)}$. Figure 13 displays some diagrams exemplifying the use of the above algorithm for finding the arguments of 6-point base functions

$$a)\ W^{(6)}_{\alpha_1^{(1)}\alpha_2^{(1)}\alpha_1^{(2)}\alpha_2^{(2)}\alpha_3^{(1)}\alpha_3^{(2)}}\left(e_1^{(1)}, e_2^{(1)}, e_2^{(1)}e_1^{(2)}, e_2^{(1)}e_2^{(2)}, e_2^{(2)}\right),$$

$$b)\ W^{(6)}_{\alpha_1^{(1)}\alpha_1^{(2)}\alpha_2^{(1)}\alpha_2^{(2)}\alpha_3^{(1)}\alpha_4^{(1)}}\left(e_1^{(1)}, e_1^{(1)}e_1^{(2)}, e_2^{(1)}e_1^{(2)}, e_2^{(1)}, e_3^{(1)}\right),$$

$$c)\ W^{(6)}_{\alpha_1^{(1)}\alpha_1^{(2)}\alpha_2^{(1)}\alpha_1^{(3)}\alpha_2^{(2)}\alpha_2^{(3)}}\left(e_1^{(1)}, e_1^{(1)}e_1^{(2)}, e_2^{(1)}e_1^{(2)}, e_2^{(2)}e_1^{(3)}, e_1^{(3)}\right). \qquad (45)$$

Concluding this section let us touch upon one more, already introduced in literature [38], way of expressing the Fourier-transforms of replica correlators (24) through *gfCC*s (12). *Nonlocal* function $X^{(n);(\omega)}$ (24) can be expressed through the corresponding principal functions entering into the expressions for *regular* functions $X^{(n)}$ (23). Consider among them the function whose indices and arguments coincide with those of function $X^{(n);(\omega)}$. Using the algorithm described in the preceding section let us write down the required functions $\tilde{\theta}^{(k)}$ in a symmetrized form through principal functions. These latter have as their arguments functions $\tilde{\lambda}(\widehat{\mathbf{q}})$ where $\widehat{\mathbf{q}}$ is a sum of some momenta of apices pertaining to different groups

$$\widehat{\mathbf{q}} = \boldsymbol{\sigma}^{(\nu_1)} + \boldsymbol{\sigma}^{(\nu_2)} + \ldots + \boldsymbol{\sigma}^{(\nu_f)}. \qquad (46)$$

Here symbol $\boldsymbol{\sigma}^{(\nu)}$ denotes the contribution into $\widehat{\mathbf{q}}$ made by the momenta from ν-th group. The rule enabling one to find principal functions for *nonlocal* correlators of individual molecules $X^{(n);(\omega)}$ from corresponding principal function for *regular* ones $X^{(n)}$ consists in replacing all arguments $\tilde{\lambda}(\widehat{\mathbf{q}})$ in the latter by products $\tilde{\lambda}(\boldsymbol{\sigma}^{(\nu_1)})\cdots\tilde{\lambda}(\boldsymbol{\sigma}^{(\nu_f)})$. Applying this procedure to all principal functions which correspond to regular correlator $X^{(n)}$ as well as allowing for the vanishing of the total momentum in every group we will get all principal functions constituting nonlocal correlator $X^{(n);(\omega)}$.

To exemplify the application of the above general algorithms, we present in the Appendix B expressions for the contributions of the first four orders to the Lifshitz entropy for an arbitrary linear copolymer written down through *gfCC*s (12).

6 Random copolymers

The algorithm outlined in the foregoing permits finding any vertex function in the Landau free energy expansion of the melt or solution of a specimen of an arbitrary linear heteropolymer provided its *gfCC*s-n (12) is known. Determination of these latter ranks among the problems
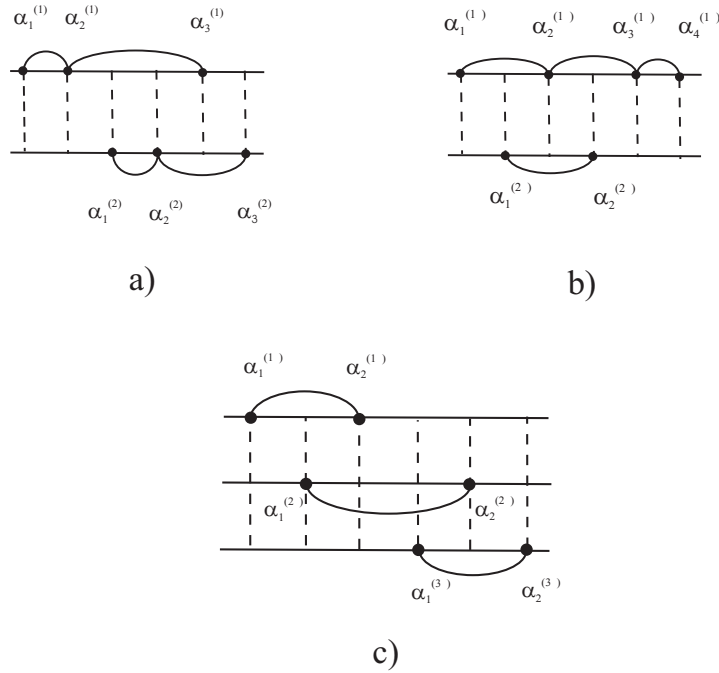
Fig. 13. Diagrams for some *gfCC*s $w^{(6)}$ of the sixth order.

of statistical chemistry of polymers [41], in the framework of which the ensemble of macromolecules is viewed as a set of realizations of a stochastic process of conventional movement along a polymer chain. For this movement transitions occur at equal intervals between regular states $S_1, \ldots, S_m$, corresponding to types $M_1, \ldots, M_m$ monomeric units, until the trajectory falls into absorbing state S_0, which corresponds to abandoning the limits of a macromolecule. The simplest among such stochastic processes with discrete time and finite number of states is the process of the Bernoulli trails [45]. Here the probability ν_α of a trajectory to reach the state S_α at any step does not depend on the states through which the trajectory passed at the preceding steps. Copolymers consisting of molecules whose sequence distribution obeys the Bernoulli statistics are referred to as random copolymers. Their *gfCC-n* (12) has the following form

$$W^{(n)}_{\alpha_1 \ldots \alpha_n}(x_1, \ldots, x_{n-1}) = X_{\alpha_n} \prod_{i=1}^{n-1} X_{\alpha_i} \Theta(x_i) \quad (47)$$

where use is made of designation

$$\Theta(x) = \left[(\nu x)^{-1} - 1 \right]^{-1},$$

$$\nu = \sum_{\alpha=1}^{m} \nu_\alpha = 1 - \nu_0 = 1 - l_{av}^{-1}. \quad (48)$$

Substituting of expression (47) into expressions (B.1, B.2, B.3, B.4) leads to expressions (see Appendix C) for the first four contributions to the

Lifshitz entropy of a random copolymer. The corresponding formulas become simpler when switching from the general thermodynamic model to the incompressible one. This is mostly because function $\tilde{\Psi}(\mathbf{q})$ (C.5) vanishes at all values of momentum $\mathbf{q}$. In this case all regular contributions to the Landau free energy are presented by formulas

$$\frac{\mathcal{F}_2^{reg}\{[\tilde{\psi}_\alpha]\}}{T} = \sum_{\alpha\beta} \left[\delta_{\alpha\beta} \frac{1}{X_\alpha} + \chi_{\alpha\beta} \right] \sum_{\mathbf{q}} \tilde{\psi}_\alpha(\mathbf{q}) \tilde{\psi}_\beta(-\mathbf{q})$$

$$\frac{\mathcal{F}_n^{reg}\{[\tilde{\psi}_\alpha]\}}{T} = (-1)^n (n-2)! \sum_{\{\mathbf{q}_i\}} \delta_K(\mathbf{q}_1 + \ldots + \mathbf{q}_n)$$

$$\times V_n(\mathbf{q}_1, \ldots, \mathbf{q}_n), \quad (n > 2),$$

$$\chi_{\alpha\beta} = (\epsilon_{\alpha\alpha} + \epsilon_{\beta\beta} - 2\epsilon_{\alpha\beta})/T \quad (49)$$

coinciding with those describing an incompressible low-molecular liquid [34]. However, the expansion of the Landau free energy of a random copolymer melt will include along with the regular contributions the non-local ones. The expressions for them are written down in terms of functions $V_n(\mathbf{q}_1, \ldots, \mathbf{q}_n)$ (C.6) and $R(\mathbf{q}) = \Theta(b(\mathbf{q}))$ (C.5). In particular, at $n = 4, 5, 6$ these expressions will read

$$\frac{\mathcal{F}_4^{nloc}\{[\tilde{\psi}_\alpha]\}}{T} = 12 \sum_{\{\mathbf{q}_i\}} \delta_K(\mathbf{q}_1 + \mathbf{q}_2) \delta_K(\mathbf{q}_3 + \mathbf{q}_4)$$

$$\times R(\mathbf{q}_{13}) V_2(\mathbf{q}_1, \mathbf{q}_3) V_2(\mathbf{q}_2, \mathbf{q}_4) \quad (50)$$

$$\mathcal{F}_5^{nloc}\{[\tilde{\psi}_\alpha]\} = 0 \quad (51)$$

$$\frac{\mathcal{F}_6^{nloc}\{[\tilde{\psi}_\alpha]\}}{T} = 360 \sum_{\{\mathbf{q}_i\}} \delta_K(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3)\delta_K(\mathbf{q}_4 + \mathbf{q}_5 + \mathbf{q}_6)$$

$$\times R(\mathbf{q}_{14})R(\mathbf{q}_{36})V_2(\mathbf{q}_1, \mathbf{q}_4)V_2(\mathbf{q}_2, \mathbf{q}_5)V_2(\mathbf{q}_3, \mathbf{q}_6)$$

$$- 240 \sum_{\{\mathbf{q}_i\}} \delta_K(\mathbf{q}_1 + \mathbf{q}_2)\delta_K(\mathbf{q}_3 + \mathbf{q}_4)\delta_K(\mathbf{q}_5 + \mathbf{q}_6)$$

$$\times R(\mathbf{q}_{135})V_3(\mathbf{q}_1, \mathbf{q}_3, \mathbf{q}_5)V_3(\mathbf{q}_2, \mathbf{q}_4, \mathbf{q}_6) \quad (52)$$

where the following designations were used

$$\mathbf{q}_{13}^2 = \mathbf{q}_1^2 + \mathbf{q}_3^2, \quad \mathbf{q}_{14}^2 = \mathbf{q}_1^2 + \mathbf{q}_4^2,$$

$$\mathbf{q}_{36}^2 = \mathbf{q}_3^2 + \mathbf{q}_6^2, \quad \mathbf{q}_{135}^2 = \mathbf{q}_1^2 + \mathbf{q}_3^2 + \mathbf{q}_5^2. \quad (53)$$

While the first of expressions (50), (51), (52) is well familiar [25], the other two have not been reported in literature.

Relationships (49, 50, 51, 52) are exact for an incompressible melt of a random copolymer with any number m of types of monomeric units. At $m = 2$, when only one parameter of order $\tilde{\psi}(\mathbf{q}) = \tilde{\psi}_1(\mathbf{q}) = -\tilde{\psi}_2(\mathbf{q})$ is involved, the second order contribution to the free energy looks as

$$\frac{\mathcal{F}_2^{reg}\{[\tilde{\psi}_\alpha]\}}{T} = \left(\frac{1}{X_1 X_2} + \chi\right) \sum_{\mathbf{q}} \tilde{\psi}(\mathbf{q})\tilde{\psi}(-\mathbf{q}),$$

$$\chi = (\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12})/T \quad (54)$$

whereas the functions $V_n(\mathbf{q}_1, \ldots, \mathbf{q}_n)$ that occur in the above expressions are determined by formula

$$V_n(\mathbf{q}_1, \ldots, \mathbf{q}_n) = \left(\frac{1}{X_1 X_2}\right)^{n-1} A_n \prod_{k=1}^{n} \tilde{\psi}(\mathbf{q}_k). \quad (55)$$

The following designations were used at expression (55)

$$A_3 = X_2 - X_1, \quad A_4 = (1 - 3X_1 X_2),$$

$$A_5 = (X_2 - X_1)(1 - 2X_1 X_2),$$

$$A_6 = 1 - 5X_1 X_2 + 5(X_1 X_2)^2. \quad (56)$$

When deriving the above formulas (49, 50, 51, 52) one has to find the coefficients $f_{\alpha_1 \ldots \alpha_n}^{*(n)}$ (8) defined by the expressions (9), (3). Since in the incompressible limit the following equality holds

$$\tilde{\Psi}(\mathbf{q}) = \sum_\alpha \tilde{\psi}_\alpha(\mathbf{q}) = \frac{\tilde{\Phi}(\mathbf{q}) - \tilde{\Phi}(\mathbf{0})\delta_K(\mathbf{q})}{Mv} \equiv 0, \quad (57)$$

so that $\tilde{\Psi}(\mathbf{q}) = \tilde{\Phi}(\mathbf{q}) = 0, (\mathbf{q} \neq 0)$ one can demonstrate that derivatives (9) of two first items in the expression (3) equal zero after convolution with the function $\tilde{\Psi}(\mathbf{q})$ and give no contribution to the free energy.

Also the importance should be also stressed of allowing for the diagonal terms in Fourier transforms of the regular and replica correlators in the incompressible limit [31]. In

such a limit $z_\alpha(\mathbf{q}) = \tilde{\psi}_\alpha(\mathbf{q})/X_\alpha$ (36), and calculating the contributions to the Lifshitz entropy one should take into account only those terms that do not contain as a factor the function $\tilde{\Psi}(\mathbf{q})$. For instance, by using the explicit expression for $gfCC$ (47) it is an easy matter to demonstrate that only the first item of the right-hand side of the expression (34) gives non-zero contribution after convolution with the components of the order parameter. Thus, neglecting the diagonal terms in functions $X^{(n)}$ leads to the vanishing of the contributions to the Lifshitz entropy for random copolymers. The omission of these terms is justified when maximal correlation length in monomer sequences along the polymer chain is large enough and is widely used for the calculation of the vertex functions for the multiblock copolymers [34].

7 Conclusions

The general diagrammatic algorithm proposed in this paper permits finding any vertex function for a specimen of linear heteropolymer with an arbitrary pattern of arrangement of monomeric units along macromolecules. An original diagram technique underlying this algorithm essentially facilitates the task of developing the computer program for the calculation of the phase diagram of melts and solutions of particular heteropolymers. This is due to the possibility to invoke computer algorithms enabling to operate directly with weighted graphs avoiding a tedious procedure of programming cumbersome analytical formulas.

Given the expressions for vertex functions of a heteropolymer specimen it is possible to construct in the framework of the Landau theory the phase diagram of its melt or solution. For the practical realization of this procedure one should use standard approaches currently available in the statistical physics of polymers [17,38].

The key role in the expansion of the Landau free energy of polydisperse polymers belongs to non-local terms describing the interaction of replicas. As far as we are concerned, dealing with such terms the authors of all preceding theoretical papers restricted their account only to the terms proportional to the forth power of the order parameter. However in the traditional Landau theory of phase transitions the addition of the subsequent items in the free energy expansion is known (see, for example, [2,46,47]) to qualitatively change the appearance of the phase diagram in hand. There are serious grounds to believe that just the same situation is the case under thermodynamic consideration of polymer liquids. This stipulates the utmost importance of the solution of the problem of finding the vertex functions whose order is more than four. Having them found by means of the algorithm put forward in the present paper one may write down the expression for the Landau free energy of a polydisperse heteropolymer liquid. This expression differing from that employed earlier by the presence of additional terms describes evidently more diverse phase behavior of polymer systems under examination.

Appendix A: Conformational and configurational averaging

In order to find regular correlator (23) it is necessary to make use of relationship (15) upon preliminary performing the Fourier transform. On doing so we will arrive at

$$\tilde{K}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n;C) = \sum_{k_1}\ldots\sum_{k_n}\prod_{i=1}^{n}\sigma_{\alpha_i}(k_i)$$

$$\times \overline{\exp\left(i\sum_{i=1}^{n}\mathbf{q}_i\mathbf{r}(k_i)\right)} \quad (A.1)$$

where indicator $\sigma_\alpha(k)$ either equals unity if the kth unit from the beginning of a polymer chain is α-type or equals zero if this is not the case. Evidently, configuration C of a linear macromolecule is unambiguously characterized by sequence $\alpha(k)$ of the values of the indicator subscript at $k = 1, 2, \ldots$ As for a macromolecule conformation, this is specified by a set of spatial coordinates $\mathbf{r}(1), \mathbf{r}(2), \ldots$ of all its monomeric units. The joint distribution of the probabilities of their coordinates defines the probability measure on the set of macromolecules' conformations. We will denote the averaging over this measure of any conformation-dependent quantity by supplying it by over-line.

Substituting expression (A.1) into formula (23) it is easy to find tensor-function $X^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n)$. The same formula may be resorted for determining tensor-function $\tilde{\theta}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n)$. For this purpose all terms should be eliminated, in which at least two of numbers $k_1,\ldots,k_n$ coincide. The remaining terms are presented as sum $n!$ of items. Each of them is a sum over all points of n-dimensional sector characterized by a particular ordered set of distinct integers $\{k_i\}$. Let us consider one of $n!$ such items corresponding to the set $k_1 < k_2 < \ldots < k_n$ which will be referred to as base set. Its contribution into $\tilde{\theta}^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n)$ looks as

$$\frac{1}{l_{av}}\sum_{k_1<k_2<\ldots<k_n}\langle\prod_{i=1}^{n}\sigma_{\alpha_i}(k_i)\rangle\overline{\exp\left(i\sum_{i=1}^{n}\mathbf{q}_i\mathbf{r}(k_i)\right)}. \quad (A.2)$$

To carry out conformational averaging of the exponent in this expression, it is convenient to have every vector $\mathbf{r}(k_i)$ written down as a sum of random vectors

$$\mathbf{r}(k_i) = \mathbf{r}(k_1) + \sum_{j=1}^{i-1}\Delta\mathbf{r}(k_j),$$

$$\Delta\mathbf{r}(k_j) = \mathbf{r}(k_{j+1}) - \mathbf{r}(k_j), \quad (A.3)$$

which for a Gaussian macromolecule are independent and, except for the first vector, normally distributed. Hence the averaging over conformations is reduced to the product $(n-1)$ of the one-dimensional Gaussian integrals taken analytically. As the result the simple expression will be arrived at

$$\overline{\exp\left(i\sum_{i=1}^{n}\mathbf{q}_i\mathbf{r}(k_i)\right)} = \delta_K(\mathbf{q}_1 + \ldots + \mathbf{q}_n)\prod_{i=1}^{n-1}(e_i)^{k_{i+1}-k_i} \quad (A.4)$$

where dependence e_i on momenta $\{\mathbf{q}_i\}$ has been defined above (35). The delta-symbol in this expression is obtained by integrating the exponent over random vector $\mathbf{r}(k_1)$ governed by spatial position of a macromolecule rather than by its conformation. On substituting relationship (A.4) into expression (A.2) and going to variables $j_i = k_{i+1} - k_i$, $i = 1,\ldots,n-1$ we will reduce expression (A.2) to the following form

$$W^{(n)}_{\alpha_1\ldots\alpha_n}\left(b^{(1)},\ldots,b^{(n-1)}\right) =$$

$$\sum_{j_1}\ldots\sum_{j_{n-1}}Y^{(n)}_{\alpha_1\ldots\alpha_n}(j_1,\ldots,j_{n-1})\prod_{i=1}^{n-1}(e_i)^{j_i} \quad (A.5)$$

where

$$Y^{(n)}_{\alpha_1\ldots\alpha_n}(j_1\ldots,j_{n-1}) =$$

$$\frac{1}{l_{av}}\sum_{k}\left\langle\sigma_{\alpha_1}(k)\ldots\sigma_{\alpha_n}\left(k + \sum_{i=1}^{n-1}(j_i+1)\right)\right\rangle. \quad (A.6)$$

This formula describes only one of $n!$ contributions corresponding to the sector $k_1 < k_2 < \ldots < k_n$. The contribution from any other sector with ordered set $k_{i_1} < k_{i_2} < \ldots < k_{i_n}$ can be also described by this formula by the rearrangement of its indices and momenta in line with the permutation $(1, 2, \ldots, n \to i_1, i_2, \ldots, i_n)$. The summation of contributions of all sectors yields the final expression for $X^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n)$, exemplified for $n = 3$ by relationship (37).

In the nonlocal case the correlator $X^{(n);(\omega)}_J$ (24) is given by expression

$$X^{(n);(\omega)}_J\left(\mathbf{q}_1^{(1)},\ldots,\mathbf{q}_{m_1}^{(1)}|\ldots|\mathbf{q}_1^{(\omega)},\ldots,\mathbf{q}_{m_\omega}^{(\omega)}\right) =$$

$$\left\{\prod_{\nu=1}^{\omega}\left(\sum_{k_1^{(\nu)}\ldots k_{m_\nu}^{(\nu)}}\right)\right\}\mathcal{G}(\{s\})\mathcal{H}(\{\mathbf{q}\}) \quad (A.7)$$

where

$$\mathcal{G}(\{s\}) = \frac{1}{l_{av}} \langle \prod_{\nu=1}^{\omega} \prod_{i=1}^{m_\nu} \sigma_{\alpha_i^\nu}(k_i^{(\nu)}) \rangle$$

$$\mathcal{H}(\{\mathbf{q}\}) = \overline{\prod_{\nu=1}^{\omega} \exp\left(i \sum_{i=1}^{m_\nu} \mathbf{q}_i^{(\nu)} \mathbf{r}(k_i^{(\nu)})\right)}. \quad (A.8)$$

Analogously to the local case, the function $\tilde{\theta}_J^{(n);(\omega)}$ can be obtained from expression (A.7) provided indices $k_i^{(\nu)}$ do not coincide one with another. This function represents the sum of $n!$ terms, with each term corresponding to a particular permutation of indices $\{k_i^{(\nu)}\}$. Evidently, among all $n!$ terms there are $N = n!/(m_1! \ldots m_\omega!)$ ones which can be obtained by intergroup permutations of indices. In turn, for each intergroup permutation there exist $(m_1! \ldots m_\omega!)$ intragroup permutations of indices. The contributions to function $\tilde{\theta}_J^{(n);(\omega)}$ resulting from intergroup and intragroup permutations of indices correspond to the base and principal $gfCC$s-n, respectively. These have been introduced in Section 5.2.

To find the arguments of base functions it is convenient to start from the permutation that answers to the following "overall" ordering of indices: $k_1^{(1)} < \ldots < k_{m_1}^{(1)} < k_1^{(2)} < \ldots < k_{m_2}^{(2)} < k_1^{(\omega)} < \ldots < k_{m_\omega}^{(\omega)}$. Taking conformational average in the expression (A.8) one finds the following explicit formula for the corresponding base function

$$W_J^{(n)}\left(e_1^{(1)}, \ldots, e_{m_1-1}^{(1)}, 1, e_1^{(2)}, \ldots, e_{m_2-1}^{(2)}, 1, \ldots,\right.$$
$$\left.\ldots, 1, e_1^{(\omega)}, \ldots, e_{m_\omega-1}^{(\omega)}\right) = \sum_{k_1^{(1)} < \ldots < k_{m_\omega}^{(\omega)}} \mathcal{G}(\{s\})$$
$$\times \prod_{\nu=1}^{\omega}\left\{\delta_K\left(\mathbf{q}_1^{(\nu)} + \ldots + \mathbf{q}_{m_\nu}^{(\nu)}\right) \prod_{i=1}^{m_\nu-1}\left(e_i^{(\nu)}\right)^{j_i^{(\nu)}}\right\}. \quad (A.9)$$

The intergroup permutations of indices $\{k_j^{(\nu)}\}$ in the expression under sign of sum (A.9) (provided $k_j^{(\nu)} < k_{j+1}^{(\nu)}$ for any $\nu = 1, \ldots, \omega$) allow one to find the arguments of the rest of base $gfCC$s. For instance, when $n = 4$, $\omega = 2$ there are six intergroup permutations which lead to the following ordering

$$1) \, k_1^{(1)} < k_2^{(1)} < k_1^{(2)} < k_2^{(2)}, \, 2) \, k_1^{(1)} < k_1^{(2)} < k_2^{(1)} < k_2^{(2)},$$
$$3) \, k_1^{(1)} < k_1^{(2)} < k_2^{(2)} < k_2^{(1)}, \, 4) \, k_1^{(2)} < k_2^{(2)} < k_1^{(1)} < k_2^{(1)},$$
$$5) \, k_1^{(2)} < k_1^{(1)} < k_2^{(2)} < k_2^{(1)}, \, 6) \, k_1^{(2)} < k_1^{(1)} < k_2^{(1)} < k_2^{(2)}$$
$$(A.10)$$

each of which corresponds to one of the six base functions presented earlier (43). In turn, the intragroup permutations of indices in every base function $gfCC$ enable one to find all $(m_1! \ldots m_\nu!)$ its principal $gfCC$s.

Appendix B: The contributions to the Lifshitz entropy expressed through gfCCs

Here we present the expressions for contributions of the first four orders to the Lifshitz entropy for an arbitrary linear copolymer written in terms of $gfCC$s (12)

$$\mathcal{S}_2^{reg}\{[\tilde{\psi}_\alpha]\} = -\sum_{\{\mathbf{q}_i\}} \delta_K(\mathbf{q}_1 + \mathbf{q}_2)$$
$$\times \left\{W_{\alpha_1}^{(1)}\delta_{\alpha_1\alpha_2} + 2W_{\alpha_1\alpha_2}^{(2)}(b_1)\right\} \prod_{k=1}^{2} z_{\alpha_k}(\mathbf{q}_k) \quad (B.1)$$

$$\mathcal{S}_3^{reg}\{[\tilde{\psi}_\alpha]\} = \sum_{\{\alpha_i\}} \sum_{\{\mathbf{q}_i\}} \delta_K(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3)\left\{W_{\alpha_1}^{(1)}\delta_{\alpha_1\alpha_2}\delta_{\alpha_2\alpha_3}\right.$$
$$+ 3[W_{\alpha_1\alpha_2}^{(2)}(b_1) + W_{\alpha_2\alpha_1}^{(2)}(b_1)]\delta_{\alpha_2\alpha_3}$$
$$\left.+ 6W_{\alpha_1\alpha_2\alpha_3}^{(3)}(b_1, b_2)\right\} \prod_{k=1}^{3} z_{\alpha_k}(\mathbf{q}_k) \quad (B.2)$$

$$\mathcal{S}_4^{reg}\{[\tilde{\psi}_\alpha]\} = \sum_{\{\alpha_i\}} \sum_{\{\mathbf{q}_i\}} \left\{\delta(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 + \mathbf{q}_4)\right.$$
$$\times \left[24W_{\alpha_1\alpha_2\alpha_3\alpha_4}^{(4)}(e_1, e_2, e_3) - 2\delta_{\alpha_1\alpha_2}\delta_{\alpha_2\alpha_3}\right.$$
$$\left.\times \left[4W_{\alpha_3\alpha_4}^{(2)}(b_3) + 4W_{\alpha_4\alpha_3}^{(2)}(b_3) + \delta_{\alpha_3\alpha_4}W_{\alpha_4}^{(1)}\right]\right]$$
$$- 12\sum_{\mu_1\mu_2} \sum_{p} \delta_K(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{p})\delta_K(\mathbf{q}_3 + \mathbf{q}_4 - \mathbf{p})$$
$$\times X_{\mu_1\mu_2}^{-1}(\mathbf{p})G_{\alpha_1\alpha_2\mu_1}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{p})$$
$$\left.\times G_{\alpha_3\alpha_4\mu_2}(\mathbf{q}_3, \mathbf{q}_4, -\mathbf{p})\right\} \prod_{k=1}^{4} z_{\alpha_k}(\mathbf{q}_k) \quad (B.3)$$

$$\mathcal{S}_4^{nloc}\{[\tilde{\psi}_\alpha]\} = -12\sum_{\{\alpha_i\}} \sum_{\{\mathbf{q}_i\}} \delta(\mathbf{q}_1 + \mathbf{q}_2)\delta(\mathbf{q}_3 + \mathbf{q}_4)$$
$$\times \left\{W_{\alpha_1\alpha_2\alpha_3\alpha_4}^{(4)}(b_1, 1, b_3) + W_{\alpha_3\alpha_4\alpha_1\alpha_2}^{(4)}(b_3, 1, b_1)\right.$$
$$+ W_{\alpha_1\alpha_3\alpha_2\alpha_4}^{(4)}(b_1, b_1b_3, b_3) + W_{\alpha_3\alpha_1\alpha_4\alpha_2}^{(4)}(b_3, b_1b_3, b_1)$$
$$+ W_{\alpha_1\alpha_3\alpha_4\alpha_2}^{(4)}(b_1, b_1b_3, b_1) + W_{\alpha_3\alpha_1\alpha_2\alpha_4}^{(4)}(b_3, b_1b_3, b_3)$$
$$+ \delta_{\alpha_2\alpha_4}\left[W_{\alpha_1\alpha_2\alpha_3}^{(3)}(b_1, b_3) + W_{\alpha_3\alpha_2\alpha_1}^{(3)}(b_3, b_1) + \delta_{\alpha_1\alpha_3}\right.$$
$$\times W_{\alpha_1\alpha_2}^{(2)}(b_1b_3) + W_{\alpha_1\alpha_3\alpha_2}^{(3)}(b_1, b_1b_3) + W_{\alpha_2\alpha_3\alpha_1}^{(3)}(b_1b_3, b_1)$$
$$\left.+ W_{\alpha_3\alpha_1\alpha_2}^{(3)}(b_3, b_1b_3) + W_{\alpha_2\alpha_1\alpha_3}^{(3)}(b_1b_3, b_3)\right] - \sum_{\mu_1\mu_2} X_{\mu_1\mu_2}^{-1}(0)$$
$$\times G_{\alpha_1\alpha_2\mu_1}(\mathbf{q}_1, \mathbf{q}_2, 0)G_{\alpha_3\alpha_4\mu_2}(\mathbf{q}_3, \mathbf{q}_4, 0)\right\} \prod_{k=1}^{4} z_{\alpha_k}(\mathbf{q}_k)$$
$$(B.4)$$

where the designations indicated at expressions (35), (36), (37) have been used and we also

denote

$$G_{\alpha_1\alpha_2\mu_1}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{p}) = \left[W^{(2)}_{\alpha_1\alpha_2}(b_1) + W^{(2)}_{\alpha_2\alpha_1}(b_1)\right]\delta_{\alpha_2\mu_1}$$
$$+ W^{(3)}_{\alpha_1\alpha_2\mu_1}(b_1, b_p) + W^{(3)}_{\alpha_1\mu_1\alpha_2}(b_1, b_2) + W^{(3)}_{\mu_1\alpha_1\alpha_2}(b_p, b_2),$$
$$G_{\alpha_3\alpha_4\mu_2}(\mathbf{q}_3, \mathbf{q}_4, -\mathbf{p}) = \left[W^{(2)}_{\alpha_3\alpha_4}(b_3) + W^{(2)}_{\alpha_4\alpha_3}(b_3)\right]\delta_{\alpha_4\mu_2}$$
$$+ W^{(3)}_{\alpha_3\alpha_4\mu_2}(b_3, b_p) + W^{(3)}_{\alpha_3\mu_1\alpha_4}(b_3, b_4) + W^{(3)}_{\mu_1\alpha_3\alpha_4}(b_p, b_4). \tag{B.5}$$

Appendix C: The contributions to the Lifshitz entropy for the random copolymer

$$\mathcal{S}_2^{reg}\{[\tilde{\psi}_\alpha]\} = -\sum_{\{\mathbf{q}_i\}}\delta(\mathbf{q}_1 + \mathbf{q}_2)\Bigg\{V_2(\mathbf{q}_1, \mathbf{q}_2) - U(\mathbf{q}_1)$$
$$\times \tilde{\Psi}(\mathbf{q}_1)\tilde{\Psi}(\mathbf{q}_2)\Bigg\} \tag{C.1}$$

$$\mathcal{S}_3^{reg}\{[\tilde{\psi}_\alpha]\} = \sum_{\{\mathbf{q}_i\}}\delta(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3)\Bigg\{\Omega_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)$$
$$+ 3\Omega_2(\mathbf{q}_1, \mathbf{q}_2)U(\mathbf{q}_3)\tilde{\Psi}(\mathbf{q}_3) + (3/2)\Omega_1(\mathbf{q}_2)$$
$$\times U(\mathbf{q}_1)U(\mathbf{q}_3)\tilde{\Psi}(\mathbf{q}_1)\tilde{\Psi}(\mathbf{q}_3)\Bigg\} \tag{C.2}$$

$$\mathcal{S}_4^{reg}\{[\tilde{\psi}_\alpha]\} = -\sum_{\{\mathbf{q}_i\}}\delta(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 + \mathbf{q}_4)$$
$$\times \Bigg\{2\Omega_4(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4) + 8\Omega_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)U(\mathbf{q}_4)v(\mathbf{q}_4)$$
$$+ 12\Omega_2(\mathbf{q}_2, \mathbf{q}_4)U(\mathbf{q}_1)U(\mathbf{q}_3)\tilde{\Psi}(\mathbf{q}_1)\tilde{\Psi}(\mathbf{q}_3)$$
$$+ (3/4)\zeta(\{\mathbf{q}_i\}; \mathbf{q}_1 + \mathbf{q}_2)\Bigg\} \tag{C.3}$$

$$\mathcal{S}_4^{nloc}\{[\tilde{\psi}_\alpha]\} = -\sum_{\{\mathbf{q}_i\}}\delta(\mathbf{q}_1 + \mathbf{q}_2)\delta(\mathbf{q}_3 + \mathbf{q}_4)\Bigg\{R(\mathbf{q}_{13})$$
$$\times Y(\mathbf{q}_1, \mathbf{q}_3)Y(\mathbf{q}_2, \mathbf{q}_4) - (1/2)U(\mathbf{q}_1)U(\mathbf{q}_3)$$
$$\times \tilde{\Psi}(\mathbf{q}_1)\tilde{\Psi}(\mathbf{q}_3)\Omega_2(\mathbf{q}_2, \mathbf{q}_4) - (3/4)\zeta(\{\mathbf{q}_i\}; 0)\Bigg\} \tag{C.4}$$

where $\mathbf{q}_{13}^2 = \mathbf{q}_1^2 + \mathbf{q}_3^2$ and we denote

$$\tilde{\Psi}(\mathbf{q}) = \sum_{\gamma=1}^m \tilde{\psi}_\gamma(\mathbf{q}), \quad R(\mathbf{q}) = \left[(\nu\tilde{\lambda}(\mathbf{q}))^{-1} - 1\right]^{-1},$$

$$U(\mathbf{q}) = 2\left(\frac{1 - \nu\tilde{\lambda}(\mathbf{q})}{1 + \nu\tilde{\lambda}(\mathbf{q})}\right)R(\mathbf{q}). \tag{C.5}$$

The following designations were also used at the expressions (C.1, C.2, C.3, C.4)

$$V_n(\mathbf{q}_1, \ldots, \mathbf{q}_n) = \sum_{\gamma=1}^m \left(\frac{1}{X_\gamma}\right)^{n-1}\prod_{k=1}^n \tilde{\psi}_\gamma(\mathbf{q}_k)$$

$$Y(\mathbf{q}_1, \mathbf{q}_3) = \frac{1}{2}\left[U(\mathbf{q}_1) + U(\mathbf{q}_3) - 2U(\mathbf{q}_1)U(\mathbf{q}_3)\right]$$
$$\times \tilde{\Psi}(\mathbf{q}_1)\tilde{\Psi}(\mathbf{q}_3) + \Omega_2(\mathbf{q}_1, \mathbf{q}_3)$$

$$\Omega_n(\mathbf{q}_1, \ldots, \mathbf{q}_n) = V_n(\mathbf{q}_1, \ldots, \mathbf{q}_n)$$
$$+ \sum_{p=1}^{n-1}(-1)^p \sum_{s_1 < \ldots < s_p}^n \left[\prod_{\nu=1}^p U(\mathbf{q}_{s_\nu})\tilde{\Psi}(\mathbf{q}_{s_\nu})\right]$$
$$\times \sum_{k_1 < \ldots < k_{n-p}(k_i \neq s_j)}^n V_{n-p}(\mathbf{q}_{k_1}, \ldots, \mathbf{q}_{k_{n-p}})$$
$$+ (-1)^n \prod_{k=1}^n U(\mathbf{q}_k)\tilde{\Psi}(\mathbf{q}_k)$$

$$\zeta(\{\mathbf{q}_i\}; \mathbf{p}) = \Big[-7U(\mathbf{q}_2)U(\mathbf{q}_4) + 4U(\mathbf{q}_2) + 4U(\mathbf{q}_4)$$
$$- U(\mathbf{p})(2 - U(\mathbf{q}_2))(2 - U(\mathbf{q}_4))\Big]U(\mathbf{q}_1)$$
$$\times U(\mathbf{q}_3)\prod_{k=1}^4 \tilde{\Psi}(\mathbf{q}_k). \tag{C.6}$$

These expressions correspond to the most general case of the compressible Bernoullian copolymer with the finite length macromolecules. It is evident that the contributions to the Lifshitz entropy for an infinite random copolymer can be found from the above expressions by equating to zero the probability of absorbing state ν_0.

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