

Ginzburg–Landau approach in the theory of polymer structures

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(Submitted 25 March 1992)

Pis'ma Zh. Eksp. Teor. Fiz. **55**, No. 10, 584–586 (25 May 1992)

The correlation functions for deformed polymer structures are calculated by the Ginzburg–Landau method for the first time.

In the standard macroscopic description of solids, the free energy F is expanded in powers of the strain tensor $u_{\mu\nu}$ (Ref. 1). This approach fails when efforts are made to describe deformed polymer structures with $u_{\mu\nu} \gtrsim 1$. In the present letter we propose a microscopic Ginzburg–Landau approach which starts with the introduction of a generalized Edwards-Anderson order parameter^{2,3}

$$\rho(\vec{R}) = \sum_{\mathbf{i}} \left\langle \prod_{k=0}^m \delta(\vec{r}_i^k - \vec{r}_i^0) \right\rangle, \quad \vec{R} = (\vec{r}^0, \dots, \vec{r}^m), \quad (1)$$

where \vec{r}_i^k are the coordinates of particle i , in equilibrium state k , and the angle brackets mean a thermodynamic average. This order parameter describes the overlap of the $k=0$ state, in which the structure was prepared, and the states $k=1, \dots, m$ under the experimental conditions. In the liquid phase there are no correlations between the coordinates \vec{r}_i^k with different values of k , and the order parameter in (1) vanishes in the thermodynamic limit. In the solid phase it remains nonzero, because the particles localize near their average positions.

As an example we consider a structure formed by random cross-linking of a chain of N units with itself. The free energy of this structure is found by a replica method,^{2–4} by taking an average of the logarithm of a partition function of the positions of the cross-links along the chain:

$$\bar{F} = dF_m\{\rho\}/dm|_{m=0}, \quad \int d\vec{R}\rho(\vec{R}) = N. \quad (2)$$

Treating $\rho(\vec{R})$ in (1) as the density of particles in a $3(1+m)$ -dimensional replica space with the coordinates \vec{R} , we can easily write an expression for the Ginzburg-Landau free energy of this replica system:

$$F_m\{\rho\} = T \int d\vec{R} \left\{ a^2 [\nabla \rho^{1/2}(\vec{R})]^2 - \frac{\beta}{2} \rho^2(\vec{R}) + \mu \rho(\vec{R}) \right\} + \sum_{k=0}^m \int d\vec{r} [f^{*k}(\rho^k(\vec{r})) + h^k(\vec{r})\rho^k(\vec{r})]. \quad (3)$$

Here we have introduced external fields h^k , which act on the monomer units in the k th replica. The gradient term in (3), which is equal to the entropy of a chain with a given density $\rho(\vec{R})$ of monomer units, was found some time ago in studies by Lifshitz.⁵ Here a is the size of a monomer unit, $-\beta\rho^2$ is the energy of the cross-linking, and the chemical potential μ is introduced in (3) in order to fix the total number of particles in (2). The interaction of the units, of density $\rho^k(\vec{r})$, in replica k is incorporated by means of the function $f^*(\rho)$, introduced by Lifshitz.⁵ This function is known from the theory of low-molecular liquids. It follows from definition (1) that $\rho^k(\vec{r})$ is given by

$$\rho^k(\vec{r}) = \prod_{l \neq k} \int d\vec{r}^l \rho(\vec{R}). \quad (4)$$

The equilibrium value of the order parameter in (1) is found by minimizing Ginzburg-Landau functional (3), (4):

$$\left(\mu + \sum_{k=0}^m \bar{h}^k(\vec{r}^k) - a^2 \nabla^2 - \beta \varphi^2 \right) \varphi = 0, \quad \varphi(\vec{R}) = \rho^{1/2}(\vec{R}), \quad (5)$$

where $\bar{h}^k = h^k + \mu^{*k}/T$ is the total field, and $\mu^{*k} = \partial f^{*k}/\partial \rho^k$ is the self-consistent field acting on the units in the k th replica. We consider a solution of Eq. (5) with a spontaneously broken translational symmetry, which is characterized (for $h^k = 0$) by a special direction in replica space:

$$\vec{e}_\mu = (1, \lambda_\mu, \dots, \lambda_\mu) / (1 + m\lambda_\mu^2)^{1/2}, \quad \mu = x, y, z. \quad (6)$$

A translation along this direction corresponds to an affine extension of the structure by a factor of λ_μ along the μ axis. A solution which is invariant under such a translation depends on only the components $\vec{R}_\mu^\perp = \vec{R}_\mu - \vec{e}_\mu(\vec{R}_\mu \vec{e}_\mu)$ of the vector \vec{R}_μ , which are perpendicular to \vec{e}_μ [see (6)]. As $m \rightarrow 0$, we find

$$\varphi_{cl}(\vec{R}) = (\tau/\beta)^{1/2} \chi[\tau(\vec{R}^\perp)^2/4a^2], \quad \tau = \mu + \mu^{*0}/T, \quad (7)$$

$$x\chi''(x) = \chi(x) - \chi^3(x), \quad \chi(0) = 1, \quad \chi(x \rightarrow \infty) = 0,$$

where τ^{-1} is the average length of the chain between neighboring cross-links. Substituting (7) into (3), we reproduce the classic result of James and Guth⁶ for the free energy of the structure, (2).

Bastide *et al.*⁷ and Mendes *et al.*⁸ have carried out experimental studies of the intensity of neutron scattering by polymer structures. This intensity is proportional to the Fourier component $G_{\vec{q}} + C_{\vec{q}}$ of the correlation function of the density fluctuations of the structures. Here G and C are the contributions of thermodynamic density fluctuations and of spatial inhomogeneities in the structures,³ given by

$$G(\vec{r} - \vec{r}') + C(\vec{r} - \vec{r}') = T^{-1} \delta^2 F_m / \delta h^1(\vec{r}) \delta h^1(\vec{r}') |_{m=0},$$

$$C(\vec{r} - \vec{r}') = T^{-1} \frac{\delta^2 F_m}{\delta h^1(\vec{r}) \delta h^2(\vec{r}')} |_{m=0}, \quad G^0(\vec{r} - \vec{r}') = T^{-1} \frac{\delta^2 F_m}{\delta h^0(\vec{r}) \delta h^0(\vec{r}')} |_{m=0}, \quad (8)$$

where G^0 is the correlation function of the density fluctuations under the conditions prevailing during the preparation of the structure.

To evaluate the correlation functions in (8), we find a solution of Ginzburg-Landau equations (5) in first order in h^k . In the long-wave limit, $\vec{q} \rightarrow 0$, both the frozen-in density fluctuations (which are deformed in an affine fashion along with the structure) and the deviations from an affine case (described by the strain vectors \vec{u}^k) contribute to $\delta\varphi$:

$$\delta\varphi(\vec{R}) \equiv \varphi(\vec{R}) - \varphi_{cl}(\vec{R}) = \frac{\partial \varphi_{cl}(\vec{R})}{\partial \mu} \sum_{k=0}^m \delta \tilde{h}^k(\vec{r}^k) - \sum_{k \neq 0, \nu} \frac{\partial \varphi_{cl}(\vec{R})}{\partial \tau_{\nu}^k} u_{\nu}^k(\vec{r}^k). \quad (9)$$

The latter are Goldstone modes for the solution of (7) with a spontaneously broken continuous symmetry [see (6)]. We find $\delta\rho^k$ as a function of h^k by substituting solutions (9) of Eqs. (5) into (4). Evaluating the derivatives in (8) with the help of this solution, and going through some simple calculations, we find

$$G_{\vec{q}} = (\kappa_{\vec{q}} + B)^{-1}, \quad C_{\vec{q}} = \kappa_{\vec{q}}^2 G_{\vec{q}}^2 \overline{n_{\vec{q}} n_{-\vec{q}}},$$

$$\overline{n_{\vec{q}} n_{-\vec{q}}} \equiv \frac{A_{\vec{q}}^2 G_{\vec{q}}^0}{\lambda_x \lambda_y \lambda_z} + \frac{2\rho}{3\tau} B_{\vec{q}}, \quad G_{\vec{q}}^0 = (\kappa_{\vec{q}}^0 + B^0)^{-1}, \quad (10)$$

where $TB^k = \partial^2 f^{*k} / (\partial \rho^k)^2$. In the limit $\vec{q} \rightarrow 0$ we have $A_{\vec{q}} = B_{\vec{q}} = 5/3$, $\kappa_{\vec{q}} = 3\tau(\lambda\vec{q})^2 / 2\rho\vec{q}^2$, and $\kappa_{\vec{q}}^0 = -\tau/\rho^0$. The vector $\lambda\vec{q}$ has the components $\lambda_{\mu} q_{\mu}$ and $\rho^0 = \rho \lambda_x \lambda_y \lambda_z$.

Expressions (10) have a simple physical meaning. The function $n(\vec{r})$ is the density distribution which maximizes the entropy of the structure, $S\{\rho\}$, of the given topological structure. Expanding S , retaining terms up to quadratic in $p - n$, and adding the energy contribution $\int d\vec{r} f^*$, we find the following expression for the free energy of this structure:

$$\frac{\Delta F\{\rho\}}{T} = \frac{1}{2} \sum_{\vec{q}} \kappa_{\vec{q}} (\rho_{\vec{q}} - n_{\vec{q}}) (\rho_{-\vec{q}} - n_{-\vec{q}}) + \frac{1}{2} \sum_{\vec{q}} B \rho_{\vec{q}} \rho_{-\vec{q}}. \quad (11)$$

Minimizing (11) with respect to $\rho_{\vec{q}}$, we find the amplitude of the spatial inhomogeneities of the structure, $\rho_{\vec{q}} = \kappa_{\vec{q}} G_{\vec{q}} n_{\vec{q}}$, which leads to expression (10) for $C_{\vec{q}}$.

As we mentioned above, $n(\vec{r})$ includes a contribution from density fluctuations $n^0(\vec{r}) = \rho^0(\lambda\vec{r})/\lambda_x\lambda_y\lambda_z$, which are frozen during the preparation of the structure, and also the fluctuations $\Delta n(\vec{r})$, which result from the deviation of the deformation from an affine nature:

$$n(\vec{r}) = \int d\vec{r}' A(\vec{r} - \vec{r}') n^0(\vec{r}') + \Delta n(\vec{r}), \quad \overline{\Delta n(\vec{r}) \Delta n(\vec{r}')} = \frac{2\rho}{3\tau} B(\vec{r} - \vec{r}'). \quad (12)$$

An evaluation of the correlation function $n(\vec{r})$ in (12) yields expression (10) for $\overline{n_{\vec{q}} n_{-\vec{q}}}$.

The correlation functions $G_{\vec{q}}$ and $C_{\vec{q}}$ in (10) depend on the direction of the wave vector \vec{q} even in the limit $\vec{q} \rightarrow 0$. This dependence, which stems from the deviations of $\vec{u}^k(\vec{r})$ in (9) from an affine nature, gives rise to the butterfly-shaped intensity contour curves, with maxima along the direction in which the structure is extended, which were observed in the experiments of Refs. 7 and 8.

I wish to thank J. Bastide and I. Ya. Erukhimovich for useful discussions.

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Translated by D. Parsons