The role of chemical reactions in the laser destruction of transparent polymers

M. A. Liberman and M. I. Tribel'skii

Institute for Physical Problems, Academy of Sciences of the USSR
(Submitted 27 June 1977)
Zh. Eksp. Teor. Fiz. **74**, 194–201 (January 1978)

A theory is developed of the optical breakdown of transparent polymers that arises from the additional absorption of light by the products of the chemical decay of the polymer, with allowance for the strong nonlinear temperature dependence of the chemical-reaction rate. The development of an instability at a small absorbing inclusion localized in the polymer matrix is investigated. This instability is of a non-threshold type. The induction time and the law of growth of the effective size of the inclusion are found. The steady-state motion of the absorption wave propagating counter to the laser radiation in the case of developed breakdown is considered. The dependences of the velocity of this wave and of the temperature behind the wave front on the parameters of the problem are found. The theory developed is applied to a quantitative explanation of the "fatigue" effects associated with repeated action of laser radiation on a sample.

INTRODUCTION

The phenomenon of optical breakdown of transparent dielectrics (i.e., the appearance of macroscopic imperfections in them under the action of sufficiently intense laser radiation) has been investigated repeatedly, both theoretically and experimentally (see, e.g., the book by Ready[1] and the literature cited in it). One explanation of the phenomenon has been the assumption of an avalanche-type instability, associated with the growth of the weak "priming" absorption of light during the action of the laser pulse and, as a consequence of this, with the loss by the medium of its original transparency. Increase in the absorption of radiation has usually been associated with an increase in the concentration of free carriers in the dielectric, occurring either as a result of the internal photoeffect and the development of an electron avalanche[1-3] or as a result of the thermal action of a random absorbing inclusion on the medium.[4]

However, besides these mechanisms of avalanche-type instabilities, additional absorption of light by the products of the chemical decomposition of the matrix material can arise under the action of laser radiation on transparent polymers. The possibility that such an instability can arise was noted in the work of Butenin and Kogan.[5]

In Ref. 6 the role of random absorbing inclusions in the optical breakdown of polymethylmethacrylate was studied. However, the chemical kinetics of the decomposition of the polymer was not considered in this work, and, as will be shown below, taking this into account alters qualitatively the character of the phenomenon.

In this paper a theory of the optical breakdown of transparent polymers is developed with allowance for the kinetics of their chemical decomposition. We shall call the phenomenon itself induction thermolysis, and the products of the chemical decomposition of the polymer, which absorb the laser radiation, we shall call carbon black, having it in mind to apply the theory to the case of an organic glass (polymethylmethacrylate),

in which the corresponding product is pure carbon.

DEVELOPMENT OF THE INSTABILITY AT AN ABSORBING INCLUSION

1. We shall consider small absorbing inclusions localized in a transparent polymer situated, from time $t = 0$, in a laser-radiation field of intensity $s_0 = $ const. For simplicity we shall suppose that the distance from the point of localization of each inclusion to the nearest boundary of the sample is large compared with the sizes of the inclusions, and this allows us to neglect the effect of heat exchange at the boundary of the sample on the formation of the temperature field near an inclusion. In addition, we shall assume that the average number density n of inclusions is sufficiently small for the temperature field near each of them to be determined by the inclusion itself (this is valid if $\bar{R}n V^{2/3} \ll 1$, where $\bar{R}$ is the mean size of an inclusion and V is the focal volume[7]). In this case we can confine ourselves to considering the phenomena that occur near any one of the inclusions. On being heated an inclusion warms up the region of the matrix adjacent to it, as a result of which chemical decomposition of the polymer (thermolysis) occurs. The carbon black released around the inclusion gives rise to further light absorption, this being equivalent to an effective increase in the size of the inclusion. This leads to increase of its temperature, which, in its turn, leads to increase in the rate of formation of carbon black, and so on.

We shall assume the absorption of radiation by the carbon black to be of the non-resonance type and describe it in the framework of geometrical optics, so that the absorption coefficient $\alpha = \alpha_0 C$, where $\alpha_0 = $ const and C is the carbon-black concentration ($0 \leqslant C \leqslant 1$). For simplicity we shall neglect the dependence on the carbon-black concentration, and also the temperature dependence, of the other parameters determining the properties of the polymer matrix.

To describe the chemical kinetics we shall use the model equation

$$\frac{dC}{dt} = \nu_0 (1-C) e^{-E/T},$$

$$C(0)=0, \quad \nu_0, \ E = \text{const.} \tag{1}$$

Everywhere below we shall be interested in the case $C \ll 1$. Then from Eq. (1) we have

$$C \approx \nu_0 \int_0^t \exp\left[-\frac{E}{T(r,t')}\right] dt'. \tag{2}$$

We approximate the initial shape of the inclusion by a sphere of radius R_0. Let t_0 be the characteristic time of development of the instability (the induction time). The case of interest is that of large t_0 ($\chi t_0 \gg R_0^2$, where χ is the coefficient of thermal conductivity of the polymer), since this case differs fundamentally from that of an ionization instability, for which the induction time is of the order of R_0^2/χ.[4] For $\chi t_0 \gg R_0^2$ a quasi-stationary temperature profile manages to become established about the inclusion, and change of this profile occurs only as a result of the effective growth, due to carbon-black formation, in the size of the inclusion.

To estimate the quantity t_0 from scaling-theory arguments we take the equation describing the temperature distribution about an inclusion[1]:

$$\varkappa \Delta T + S \alpha_0 \nu_0 \int_0^t \exp\left[-\frac{E}{T(r,t')}\right] dt' = 0, \tag{3}$$

where $\varkappa$ is the thermal conductivity of the polymer and S is the local value of the intensity of the laser radiation. In this case the characteristic length over which the temperature varies is R_0, and the characteristic temperature is the initial temperature T_0 of the inclusion before the carbon black begins to form:

$$T_0 = \frac{\sigma(R) S_0}{4\pi \varkappa R_0} = \frac{R_0 S_0}{4\varkappa}, \tag{4}$$

where $\sigma(R)$ is the cross-section for absorption of radiation by the inclusion. The latter equality in (4) is written for a perfectly black sphere, as the inclusion will be assumed to be in the following.

Introducing $\Theta \equiv T/T_0$ and $z \equiv r/R_0$, we transform (3) to the form

$$\Delta \Theta + \Lambda_0 s \int_0^t \nu_0 e^{-1/\Theta} dt' = 0, \tag{5}$$

where

$$s = 4S/S_0, \quad \gamma = E/T_0, \quad \Lambda_0 = \alpha_0 R_0.$$

We note, since we shall need this in the following, that Eq. (1) has physical meaning only so long as $T \ll E$; therefore, γ is always large compared with unity.

Taking into account that $|\Delta\Theta| \sim s \sim 1$ for $z \sim 1$, and $\Theta(1,t) \sim 1 + t/t_0$, we obtain from (5) that

$$t_0 = \gamma e^{\gamma} / \Lambda_0 \nu_0. \tag{6}$$

2. We shall consider the wave of carbon-black for-

mation propagating from the inclusion. We note that in the initial stage such a wave will possess spherical symmetry even in the case when R_0 is large compared with the wavelength of the radiation. This is due to the slowness of the process of carbon-black formation compared with the thermal conduction, which symmetrizes the problem.

The equation of absorption of the light flux will be

$$\frac{dS}{dr} = -\alpha_0 C(r,t) S.$$

Treating the wave of carbon-black formation propagating from the nucleus as a discontinuity surface, i.e., assuming that all the light flux is absorbed at the front of such a wave, we obtain the following equation for the radius R of the wave front:

$$\Lambda(t) = \alpha_0 \int_R^\infty C(r,t) dr = 1. \tag{7}$$

We substitute the expression (2) into Eq. (7) and use for $T(r,t)$ the approximation

$$T(r,t) = \begin{cases} T(R) R/r & \text{for} \quad r \geqslant R(t), \\ T(R) & \text{for} \quad r \leqslant R(t), \end{cases} \tag{8}$$

where $T(R)$ is defined by (4) with R_0 replaced by $R(t)$.

Taking into account that $C(r,0)=0$, we conclude that Eq. (7) has a solution only for $t \geqslant t_0$, where t_0 is the time the absorption wave front breaks away from the surface of the inclusion. For $t \leqslant t_0$ we have $R(t) = R_0$. Hence we immediately obtain for t_0 the expression (6). For $t \geqslant t_0$ we have

$$\Lambda(t) = \Lambda_0 \nu_0 \int_y^\infty dz \int_0^t \exp\left[-\gamma \frac{z}{y^2(t')}\right] dt', \tag{9}$$

where $y = R/R_0$ and z, Λ_0 and γ are defined above.

In the expression (9) we change the order of integration and break the integral into two parts: from 0 to t_0 and from t_0 to t. The first of these is taken in quadratures. In the second we change from the variable t' to y, after which dt/dy is taken outside the integral as a function that is slowly varying compared with the exponential remaining under the integral. The integral obtained as a result of these transformations is calculated in the standard way. As a result, the equation determining the motion of the front of the wave of carbon-black formation acquires the form

$$\frac{dy}{dx} = \frac{e^{1-1/y}}{2\gamma} y^4 \frac{1 - \exp[-2\gamma(y-1)/y^2]}{1 - \exp[-\gamma(y-1)]},$$

$$y(x \leqslant 1) = 1, \tag{10}$$

where $x = t/t_0$.

Equation (10) can be integrated numerically. The results of these calculations for different values of γ are given in Fig. 1.

To investigate the general laws of the development of the instability it is worthwhile to given an approximate
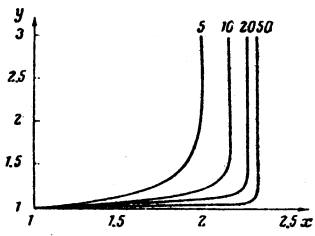
FIG. 1. Growth of the effective size $y \equiv R/R_0$ of an inclusion with time $x \equiv t/t_0$ for different values of the parameter γ. The values of γ are denoted by the figures above the corresponding graphs.

analytic solution of Eq. (10). This is straightforward to obtain if we take into account that the factor to the right of y^4 differs from unity only in the small region $y - 1 \lesssim \gamma^{-1}$. Expanding the arguments of the exponentials in powers of $y - 1$ in this region and replacing the whole fraction by unity for $y - 1 > \gamma^{-1}$, we obtain

$$y = 1 - \gamma^{-1} \ln(2\exp[-\tfrac{1}{2}(x-1)] - 1) \tag{11}$$

for $1 \leq x \leq 1.761$, and

$$y = \gamma(\ln[\tfrac{1}{2}(x_\infty - x)\gamma^2 e^\gamma] - 2\ln\ln[\tfrac{1}{2}(x_\infty - x)\gamma^2 e^\gamma] + \ldots)^{-1} \tag{12}$$

for $x \geq 1.761$, where $x_\infty = 2.496 - 2.206/\gamma + O(1/\gamma^2)$ \tag{13}

and satisfies the condition $y(x_\infty) = \infty$. The asymptotic form (12) is valid up to $x - x_\infty \sim \gamma^{-2}e^{-\gamma}$, i.e., practically up to the region in which $y(x)$ becomes infinite.

It follows from the expression (13) that the effective size of the inclusion goes to infinity in an explosive manner in a time differing from t_0 by a numerical factor of order unity, i.e., t_0 is the only characteristic time in the problem.

We note also that the carbon-black concentration in the front of the wave of carbon-black formation decreases monotonically with increase of the effective size of the inclusion and is a maximum at the time the front breaks away from the surface of the bare inclusion, i.e., at $t = t_0$.

STEADY-STATE MOTION OF THE WAVE OF CARBON-BLACK FORMATION

As the rate of growth of the effective size of the inclusion increases the problem loses its spherical symmetry, since the heat conduction does not have time to equalize the angular components of the temperature gradient. As a result of this the wave front of carbon-black formation acquires a different velocity at different points, the part with the maximum velocity being that propagating counter to the laser radiation. The final result of these processes is that the wave of carbon-black formation is transformed into a plane wave propagating counter to the laser radiation. It is of interest to investigate the dependence of the velocity of the steady-state motion of this wave, and of the temperature behind its front, on the parameters of the problem.

The equations describing the steady-state motion of the wave in the coordinate frame moving with the wave front have the form

$$\rho c_p u \frac{dT}{d\xi} = \frac{d}{d\xi}\left(\varkappa \frac{dT}{d\xi}\right) - \frac{dS}{d\xi}, \tag{14}$$

$$\frac{dS}{d\xi} = -\alpha_0 C S, \tag{15}$$

where u is the velocity of the wavefront, and ρ is the density and c_p the specific heat of the polymer. Taking into account that $dt = d\xi/u$, we rewrite (2) in the form

$$C = \frac{v_0}{u} \int_{-\infty}^{\xi} \exp\left[-\frac{E}{T(\xi')}\right]d\xi' = \frac{v_0}{u} \int_0^T \frac{d\xi}{dT'}\exp\left[-\frac{E}{T'}\right]dT'. \tag{16}$$

The system (14)–(16) must be supplemented by the boundary conditions

$$T(-\infty) = 0, \quad \frac{dT}{d\xi}(-\infty) = 0, \quad S(-\infty) = S_0,$$

$$T(\infty) = T_\infty, \quad \frac{dT}{d\xi}(\infty) = 0, \quad S(\infty) = 0. \tag{17}$$

By means of the conditions (17) all the integration constants and the velocity of the wave front are determined.

Henceforth we proceed in the standard way.[8] With the boundary conditions taken into account, the first integral of Eq. (14) has the form

$$\rho c_p u T = \varkappa \frac{dT}{d\xi} - S(\xi) + S_0. \tag{18}$$

Letting $\xi \to \infty$, from (18) we obtain the conservation law

$$\rho c_p u T_\infty = S_0. \tag{19}$$

It follows from (16) that the main change of S occurs in the region in which the temperature is hardly varying and is close to its maximum value $T = T_\infty$. Therefore, (18) can be written approximately in the form

$$\varkappa \frac{dT}{d\xi} = S(\xi). \tag{20}$$

Integrating the right- and left-hand sides of (15) with respect to ξ with allowance for (17) and using (20) to change from integration over ξ to integration over T in the left-hand side, we obtain

$$S_0 = \int_0^{T_\infty} \alpha_0 \varkappa C(T, u) dT. \tag{21}$$

We substitute (16) into (21), change the order of integration, and take $d\xi/dT$ outside the integral, taking into account that, in the zeroth approximation, the region of liberation of energy can be assumed to be the discontinuity surface, on which the relation $\varkappa dT/d\xi = S_0$ is fulfilled. Finally, we obtain

$$S_0 = \alpha_0 \frac{v_0}{u} \frac{T_\infty^4}{E^2} \frac{\varkappa^2}{S_0} \exp\left[-\frac{E}{T_\infty}\right]. \tag{22}$$

Equations (19) and (22) fully solve the formulated problem. In explicit form the dependences of interest to us are

M. A. Liberman and M. I. Tribel'skiĭ

$$T_\infty = E/g, \quad u = S_0 g / c_p \rho E, \tag{23}$$

where g is the solution of the transcendental equation

$$g^2 e^g = (S_E / S_0)^3, \quad S_E = \alpha_0 \varkappa E (\nu_0 / \alpha_0^2 \chi)^{\frac{1}{2}}, \tag{24}$$

equal to

$$g = \ln(S_E / S_0)^3 - 5 \ln \ln \left(\frac{S_E}{S_0} \right)^3 + \dots . \tag{25}$$

We remark that in treating the development of breakdown at an absorbing inclusion we have not taken into account the possibility of the appearance of an ionization instability.[4] Since, for fixed S_0, such an instability has a threshold with respect to the quantity R_0 (for $R_0 < \bar{R}(S_0)$ the instability does not arise), we have tacitly assumed here that the initial size of the inclusion is less than $\bar{R}(S_0)$. Even if the effective size of the inclusion did exceed $\bar{R}(S_0)$ during its growth as a result of carbon-black formation, this could not substantially change either t_∞ or, a fortiori, t_0 ($t_\infty = x_\infty t_0$ is the total time of development of the process), since the ionization halo gives little extra absorption of light up to the moment of onset of the instability.

However, in studying the motion of the absorption wave we should take into account that, alongside the wave of carbon-black formation, an absorption wave due to ionization is also possible. The propagation of such a wave through a condensed dielectric was investigated in Refs. 9 and 10. The radiation-absorption coefficient in this case is equal to $\beta_0 e^{-I/T}$, where I is half the ionization potential. The dependence of u and T_∞ on the parameters of the problem in the case of an ionization wave has the same form as (23), but with a different value of g. The corresponding formulas are given in Refs. 9 and 10.

Assuming that u and T_∞ are determined by one of these mechanisms and taking the other into account by perturbation theory, we compare the width l_c of the energy-liberation zone for the wave of carbon-black formation ($l_c \sim (\alpha_0 C_\infty)^{-1}$, where C_∞ is the concentration of carbon black immediately behind the wavefront) with the corresponding width $l_I \sim \beta_0^{-1} \exp(I/T_\infty)$ for the ionization wave. The criterion for selection of one or the other mechanism of propagation of the absorption wave will be the condition $l_c \ll l_I$ (or $l_c \gg l_I$). It turns out that for $I > E/3$ only a wave of carbon-black formation is possible. If, however, $I < E/3$, two characteristic values, S_c and S_I, of the laser-radiation intensity arise in the problem. The absorption is due to an ionization wave for $S_0 \ll S_I$ and due to a wave of carbon-black formation for $S_0 \gg S_c$.
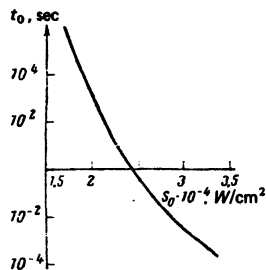
FIG. 2. Dependence of the induction time on the laser-radiation intensity for an inclusion of size 5×10^{-4} cm, localized in an organic glass (polymethylmethacrylate).

In the general case the expressions for S_I and S_c have an extremely cumbersome form; therefore, we give only the formula for S_c for[2] $I \ll E$. We have

$$S_c = S_E \frac{\beta_0}{\alpha_0} \left(\frac{\alpha_0^2 \chi}{\nu_0} \right)^{\frac{1}{2}} = \beta_0 \varkappa E. \tag{26}$$

DISCUSSION OF THE RESULTS. NUMERICAL ESTIMATES

1. We give here some numerical estimates for polymethylmethacrylate, for which $\kappa = 2.1 \times 10^{-3}$ W/cm. deg, $\chi = 1.2 \times 10^{-3}$ cm²/sec, $\rho = 1.2$ g/cm³. For ν_0, α_0 and E we take the values $\nu_0 = 10^{13}$ sec⁻¹, $\alpha_0 = 10^5$ cm⁻¹ (the absorption coefficient of pure carbon in the visible and near-infrared region), and $E = 3.84$ eV (the C-C bond energy).

Figure 2 shows the dependence, calculated from formula (6), of the induction time for an absorbing inclusion with initial size $R_0 = 5 \times 10^{-4}$ cm ($R_0^2 / \chi = 2.1 \times 10^{-4}$ sec). We note that, although induction thermolysis does not have a threshold for the onset of instability, for values of S_0 that are too small the induction time becomes so long that for practicable durations of the action of the laser radiation the instability does not arise. In view of the exponential dependence of t_0 on E and the absence of data on the exact value of the latter, the estimates given for the induction time must be taken more as an illustration of the theory developed than as an attempt to predict the experimental values. For the wave of carbon-black formation, for $S_0 = 3 \times 10^4$ W/cm² we have $T_\infty = 3.25 \times 10^3$ K and $u = 5.3$ cm/sec (we emphasize the extremely small values of the velocity of propagation of the wave of carbon-black formation, which is characteristic for the problem under consideration).

2. The entire analysis carried out above pertains to the case of a laser operating in either the continuous or mono-pulse regime. We note, however, that carbon-black formation is an irreversible process. Therefore, if the action of the radiation is interrupted at a certain time $t < t_\infty$, and then restored after any arbitrarily long time interval, the development of the instability will proceed just as if the laser pulse had not been interrupted at all (transient processes associated with cooling and heating of the inclusion can be neglected, since the corresponding characteristic time is short compared with t_0).

It follows from what has been said that the theory developed can be applied without substantial changes to explain the "fatigue" effects that arise on repeated action of laser radiation on a sample. In particular, if the laser operates in the frequency regime with pulse duration $\tau \gg R_0^2 / \chi$, for estimating the "resource" of a sample, i.e., the number N of pulses that a sample can withstand without being destroyed, we have the expression

$$N \sim \frac{t_0}{\tau} = \frac{\gamma e^\gamma}{\Lambda_0 \nu_0 \tau}. \tag{27}$$

In view of the exponential dependence of t_0 on S_0 (cf. (4), (5)), the resource of the sample should increase sharp-

M. A. Liberman and M. I. Tribel'skiĭ   102

ly when the laser-radiation intensity is decreased by a comparatively small amount, in agreement with the experimental data of Ref. 5.

The authors are grateful to A. V. Butenin and B. Ya. Kogan for kindly providing them with the results of an experimental investigation of the optical breakdown of polymers.

[1)] Estimates show that the energy contribution made by chemical reactions to the energy balance is negligibly small.

[2)] We note that, generally speaking, the relationship between I and E can vary in wide limits, since the polymer chain can have side branches possessing either a small ionization potential (but with no tendency to carbon-black formation) or the opposite properties.

[1]J. F. Ready, Effects of High-power Laser Radiation, Academic Press, N.Y., 1971 (Russ. transl., Mir, M., 1974).

[2]T. P. Belikova and E. A. Sviridenkov, Pis'ma Zh. Eksp. Teor. Fiz. 1, No. 6, 37 (1965) [JETP Lett. 1, 171 (1965)].

[3]P. M. Mednis and V. M. Faĭn, Zh. Eksp. Teor. Fiz. 62, 812 (1972) [Sov. Phys. JETP 35, 429 (1972)].

[4]A. V. Butenin and B. Ya. Kogan, Kvantovaya Elektron. (Moscow) No. 5, 143 (1971) [Sov. J. Quantum Electron. 1, 561 (1971)]; S. I. Anisimov and B. I. Makshantsev, Fiz. Tverd. Tela 15, 1090 (1973) [Sov. Phys. Solid State 15, 743 (1973)].

[5]A. V. Butenin and B. Ya. Kogan, Kvantovaya Elektron, (Moscow) 3, 1136 (1976) [Sov. J. Quantum Electron. 6, 611 (1976)].

[6]A. A. Kovalev, B. I. Makshantsev, B. F. Mul'chenko and N. F. Pilipetskiĭ, Zh. Eksp. Teor. Fiz. 70, 132 (1976) [Sov. Phys. JETP 43, 69 (1976)].

[7]M. I. Tribel'skiĭ, Kvantovaya Elektron. (Moscow) 3, 2374 (1976) [Sov. J. Quantum Electron. 6, 1293 (1976)].

[8]Yu. P. Raĭzer, Lazernaya iskra i rasprostranenie razryadov (The Laser Spark and the Propagation of Discharges), Nauka, M., 1974, Chapter 6.

[9]P. S. Kondratenko and B. I. Makshantsev, Zh. Eksp. Teor. Fiz. 66, 1734 (1974) [Sov. Phys. JETP 39, 851 (1974)].

[10]M. I. Tribel'skiĭ, Fiz. Tverd. Tela 18, 1347 (1976) [Sov. Phys. Solid State 18, 775 (1976)].

Translated by P. J. Sheperd

Possibility of a second-order transition under liquid-crystal ordering

E. E. Gorodetskiĭ and V. M. Zaprudskiĭ

All-Union Research Institute of Physicotechnical and Radiotechnical Measurements

A model with a tensor order parameter is considered; it describes, in particular, transitions from an isotropic liquid to a nematic liquid crystal. It is shown that despite the presence of cubic invariants in the Hamiltonian, the system may undergo a second-order phase transition.

PACS numbers: 64.70.Ew

A well-known result of Landau's theory of phase transitions asserts that in the presence of cubic invariants in the Hamiltonian of the system, second-order phase transitions are possible only at isolated points of the phase diagram (corresponding to the vanishing of the cubic terms). In the present paper we shall show that allowance for fluctuations leads to the result that even when threefold invariants are present in the Hamiltonian, second-order phase transition are nevertheless possible.

We consider a system in which a phase transition is described by a tensor order parameter Q_{ij}. We suppose that Q_{ij} is a symmetric tensor with zero trace. It is this situation that occurs, for example, in transitions from an isotropic liquid to a nematic liquid crystal. The Hamiltonian in this case has the form[1]

$$H = \tau Q^2 + \lambda Q^3 + u Q^4 + k^2 Q^2. \tag{1}$$

Here Q^2, Q^3, and $Q^4 = \frac{1}{2}(Q^2)^2$ are invariants of the second, third, and fourth orders, and $k^2 Q^2$ is a symbolic description of a gradient term.

Near a phase-transition point, determined by the condition $\tau = 0$, the singularities of all thermodynamic quantities are expressed in terms of Green's function and the complete renormalized threefold and fourfold vertices $\tilde{\lambda}$ and $\tilde{u}$.[2] The expansion of the complete vertices $\tilde{\lambda}$ and $\tilde{u}$ as series in the bare constants

$$\lambda \equiv -\!\!\prec \quad , \qquad u \equiv \times \tag{2}$$

has the form

$$\tilde{u} \equiv \rlap{)(}\times = \times + \bowtie + \rlap{)}\!\!\prec\!\! + \rlap{\square}{} + \cdots , \tag{3}$$

$$\tilde{\lambda} \equiv -\!\!\!\ll = -\!\!\prec + -\!\!\!\ll\!\! + -\!\!\!\lessdot + \cdots .$$

The solid lines in these expressions denote the renormalized Green's function $G(k) = (k^2 + r_c^{-2})^{-1}$ (r_c is the correlation radius). Here and below, we shall set equal to zero the critical index η, which describes the deviation of the correlation function from the Ornstein-Zernke form.

To calculate the threefold and fourfold vertices, we shall use a method proposed by S. L. Ginzberg.[3] This

0038-5646/78/4701-0103$02.40