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EQUILIBRIUM AGGREGATION IN A MODERATELY CONCENTRATED FINELY DISPERSED SYSTEM

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The equilibrium properties of dispersed small interacting particles capable of reversible aggregation are investigated.

The aggregation and structurization of a finely dispersed system can lead to changes in its physical characteristics (effective viscosity, thermal and electrical conductivities, etc.) by more than one or two orders. The shape and structure of the aggregates formed depend on the interaction between the particles of the dispersion, and if the interaction is central fairly coarse aggregates can be regarded as approximately spherical. Below we consider a system of spherical aggregates in a state of detailed balance with one another and with single particles. We ignore the formation of structures by the aggregates, which is possible in a concentrated system. This restricts the analysis to reversible aggregation processes in moderately concentrated systems.

Attempts to apply the techniques of equilibrium statistical mechanics to the investigation of such systems are rather rare [1-6]. The intrinsic volume of the particles is usually ignored in this case [1-5], which does not allow the examination of a highly concentrated system; some critical comments on [1-4] are made in [6]. We adopt here the method of [6], based on the use of a lattice model of the type introduced in [7] and suitable for the analysis of concentrated systems; we also correct the inaccuracies in [6].

General Relations. Assuming that the states of a particle system with different "occupation numbers" ν_i are distinguishable, we determine the total number of possible states of the system by the relation [6]

$$W(\nu_i)=\frac{M!}{(M-N)!\;N!}\;\frac{N!}{\prod\limits_i N_i!}\;\prod_i\frac{N_i!}{(i!)^{\nu_i}\,\nu_i!\;M^{\nu_i(i-1)}}\,, \tag{1}$$

where

$$M=\frac{V}{(v/\rho_a)}=\frac{\rho_a}{\rho}\,N,\;\;N=\sum_i N_i\,,\;\;N_i=i\nu_i\,. \tag{2}$$

The first, "configurational," cofactor in (1) is equal to the number of ways in which N indistinguishable particles can be arranged in a lattice with M cells of the same type [7]; the second, "conformational," cofactor represents the number of ways in which N particles can be distributed among "aggregate phases" with N_i particles; the third factor is the number of ways in which the particles of these phases can be distributed among different aggregates, with due allowance for the constraint effects manifested when particles which are not free but are bound into aggregates are arranged in a lattice (see [8] also). In [2] the quantity W was mistakenly identified only with the second cofactor in (1), in [5] the configurational contribution to W was completely ignored, and in [6] the Boltzmann factor

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$(N!)^{-1}$, which takes into account the a priori indistinguishability of the particles, was omitted without any justification.

Taking the energy of a system of single, noninteracting particles as zero energy, we write

$$U(\nu_i) = \sum_i E_i \nu_i = \sum_i (-\varepsilon' + \varepsilon_i)\, i\nu_i = -\varepsilon' N + \sum_i \varepsilon_i N_i, \tag{3}$$

where the energy "surface defect" ε_i characterizes (for one particle) the "degree of unsaturation" of the interparticulate bonds in an aggregate due to the fact that some of the particles comprising the aggregate are situated on its surface and not within it. We have

$$\begin{gathered} \varepsilon_1 = \varepsilon',\ \varepsilon_2 = \varepsilon' - \Delta\varepsilon,\ \ldots,\ i\varepsilon_i = \varepsilon f(i) \approx 4\,\varepsilon i^{2/3}\ (i \gg 1), \\ \varepsilon' = z'\Delta\varepsilon,\ \varepsilon = (z' - z'')\,\Delta\varepsilon. \end{gathered} \tag{4}$$

For small i (>2) ε_i is not single-valued — its value depends on the total number of interparticulate bonds in the particular aggregate. For instance, in the case of $i = 3$ for an aggregate in the form of a chain with two such bonds $\varepsilon_3 = \varepsilon' - (2/3)\Delta\varepsilon$, and for a cluster with three bonds $\varepsilon_3 = \varepsilon' - \Delta\varepsilon$. Thus, in a fuller analysis we would have to distinguish between aggregates of different types, but of the same size, by introducing appropriate numbers ν_i', ν_i'', ... We note also that the "internal" variables, which characterize the state of single particles, are not taken into consideration.

The statistical sum of the system, characterizing its properties, which are completely described by the set of numbers ν_i', is written in the well-known "main term" approximation in the form

$$Z(\nu_i) = W(\nu_i) \exp[-U(\nu_i)/kT]. \tag{5}$$

Using the Stirling formula for the factorials of large numbers and taking (1) into account, we obtain at the "thermodynamic limit" ($N \to \infty$, $N_i/N = n_i$) the following expression for the entropy of the system:

$$\begin{gathered} S = k \ln W = S_0 + \Delta S,\ \Delta S = \Delta_1 S + \Delta_2 S, \\ S_0 = -Nk\left[\ln \frac{\rho}{\rho_a} + \left(\frac{\rho_a}{\rho} - 1\right) \ln\left(1 - \frac{\rho}{\rho_a}\right)\right], \\ \Delta_1 S = -Nk \sum_i n_i \ln n_i,\ \Delta_2 S = Nk \sum_i n_i \left[n_i\left(1 - \frac{1}{i}\right) \ln\left(\frac{n_i}{i}\ \frac{\rho}{\rho_a}\right) + \left\{\ln i - \left(1 - \frac{1}{i}\right) - \frac{1}{i} \ln(i!)\right\}\right]. \end{gathered} \tag{6}$$

The terms S_0, $\Delta_1 S$, and $\Delta_2 S$ in this expression correspond to the different cofactors in formula (1); when $i \gg 1$ the quantity in the braces in (6) is approximately equal to $(\ln\sqrt{2\pi i} + 0.5)/i$. The entropy S_0 of a system of single particles decreases from infinity for a maximally diluted system ($\rho \to 0$), whose particles can be found in an infinitely large number of states, to zero for a closely packed system ($\rho \to \rho_a$), which can obviously be found in a single state that can be distinguished within the framework of the adopted lattice model. The entropy of aggregation ΔS is negative when $0 < \rho < \rho_a$, which reflects the increase in order of the system due to its aggregation.

Using (3) and (6) it is easy to determine all the other thermodynamic functions of the system. For instance, the Helmholtz free energy is expressed as follows:

$$F = U - TS = F_0 + \Delta F,\ F_0 = -TS_0,\ \Delta F = U - T\Delta S, \tag{7}$$

where F_0 relates to a system of single particles and is purely entropic, while ΔF characterizes the change in free energy due to aggregation.

The chemical potential of a particle in an aggregate of i particles is

$$\begin{gathered} \mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,M} = \mu_0 + \Delta\mu_i;\ \mu_0 = -kT \ln\left(\frac{\rho_a}{\rho} - 1\right), \\ \Delta\mu_i = -\varepsilon' + \varepsilon_i + \frac{kT}{i} \ln\left[\frac{n_i(i!)}{i} \left(\frac{\rho}{\rho_a}\right)^{1-i}\right]. \end{gathered} \tag{8}$$

[In the derivation of (8) the equivalence of the conservation of volume condition to the condition M = const, and the formulas (3)-(7), and $N = \Sigma N_i$, were taken into account.]

Minimizing F from (7) with N = const we obtain expressions for the numbers ν_i [6]:

$$\nu_i = \frac{M}{i!} \exp[(\alpha - \beta_i) i], \ \beta_i = \frac{\varepsilon_i}{kT}, \ \beta = \frac{\varepsilon}{kT}, \tag{9}$$

$$\beta_i = \beta f(i)/i \approx 4\beta i^{-1/3} \ (i \gg 1),$$

where α has the sense of activity and is given by the equation [see (8)]

$$J = \sum_i \frac{1}{(i-1)!} \exp[(\alpha - \beta_i) i] = \frac{N}{M} = \frac{\rho}{\rho_a}. \tag{10}$$

From (9) we obtain formal expressions for β_i (or ε_i) in terms of α and ν_i and, by using these in (8), we obtain

$$\mu_i = \mu_0 + kT(\alpha - \beta' - \ln(\rho/\rho_a)), \ \beta' = \varepsilon'/kT. \tag{11}$$

The independence of μ_i on i reflects the law of mass action, which holds for many other systems in a state of associative equilibrium [9]. From this it is easy to obtain the usual thermodynamic corollaries of the Dalton law type for the partial pressures of the aggregate phases, and so on.

Finally, we give the formula connecting the radius of large aggregates with the number i [2, 6]:

$$i = \left(\frac{R_i}{r} - 1\right)^3 + 4\left(\frac{R_i}{r}\right)^2, \ r = \frac{a + l}{\rho_a^{1/3}}, \ i \gg 1. \tag{12}$$

The terms in this expression give the numbers of particles within the aggregate and on its surface; at very large i the asymptotic formulas $R_i \approx ri^{1/3}$, $f(i) \approx 4i^{2/3}$ are true [the latter expression was used in (4) and (9)].

Investigation of Aggregate Equilibrium. As numerous experiments indicate, and as the theory in [6] confirms, two fundamentally different situations are possible. If the value of ε for fixed ρ/ρ_a and T is not too high, the system contains mainly single particles (singlets) and a much smaller number of doublets, triplets, and other aggregates of several particles. In this case the terms of the sum in (10) decrease rapidly with increase in the number i. If ε is greater than a certain critical value ε_*, which depends on ρ/ρ_a and T, the system is a suspension of very large aggregates in a dilute system of single particles with a small admixture of doublets, triplets, etc. The "remote" maximum of the terms of the sum in (10), attained at a certain $i = i_m \gg 1$, corresponds to this situation.

If this maximum actually exists, then α, β, and i_m will satisfy the following equation and inequality:

$$\alpha = \beta f'_m + \ln i_m - \frac{1}{2i_m}, \ \beta f''_m + \frac{1}{i_m}\left(1 + \frac{1}{2i_m}\right) > 0, \tag{13}$$

$$f'_m = df/di, \ f''_m = d^2f/di^2, \ i = i_m.$$

For an approximate solution of Eq. (10) we calculate the sum J, taking into account that if the remote maximum is present a significant contribution to it is made, firstly, by terms with small i and, secondly, by terms with $i \approx i_m$, i.e., $J \approx J_1 + J_2$. The calculation of the sum J_1 of the first terms is hindered by the fact that within the framework of the developed theory the energy ε_i for small aggregates cannot be determined uniquely. Hence, we confine ourselves here to obtaining upper and lower estimates of J_1.

For ε_i the inequality $\varepsilon i < \varepsilon_i i < \varepsilon' i - \Delta\varepsilon(i - 1)$ is valid. The estimate $\varepsilon_i \approx \varepsilon$ underestimates the total energy of particles in small aggregates — it is assumed, in fact, that these particles on the average involve the same number of interparticulate bonds as particles in large aggregates. The estimate $\varepsilon_i \approx \varepsilon' - ((i - 1)/i)\Delta\varepsilon$, on the other hand, overestimates the energy of the particles — it is assumed that in small aggregates the number of interparticulate bonds is the lowest possible, i.e., these aggregates consists of linear chains of particles. Using these limiting estimates, we obtain after simple calculation

$$\begin{aligned}\sup J_1 &\approx \sum_{i=1}^{\infty} \frac{1}{(i-1)!} \exp[(\alpha-\beta) i] = \exp\{\alpha-\beta+\exp(\alpha-\beta)\},\\ \inf J_1 &\approx \sum_{i=1}^{\infty} \frac{1}{(i-1)!} \exp[(\alpha-\beta') i + \Delta\beta(i-1)]\\ &= \exp\{\alpha-\beta'+\exp(\alpha-\beta'+\Delta\beta)\},\ \Delta\beta = \Delta\varepsilon/kT.\end{aligned} \tag{14}$$

The formula for sup J_1 was previously obtained in [6]. Usually $z' = 6\text{–}8$, $z'' = 5\text{–}6$, i.e., from (4) $\beta = (1\text{–}2)\Delta\beta$, $\beta' = (6\text{–}8)\Delta\beta$.

An idea of the lower limits of quantities ε_* and i_m can be obtained by noting that when $J_1 \approx$ sup J_1 it follows from (10) that $\alpha-\beta < 0$. From this and (13), neglecting $1/i_m$ in comparison with unity, we obtain a double inequality that is a necessary (but not sufficient) condition for the appearance of large aggregates in the system:

$$(1-f'_m)^{-1} \ln i_m \lesssim \beta \lesssim (i_m |f''_m|)^{-1}. \tag{15}$$

Using the asymptotic form $f(i) \approx 4i^{2/3}$ we see that the right-hand side of (15) is, in fact, larger than the left-hand side when $i_m \gtrsim 575$, to which $\beta \gtrsim 9.35$ corresponds.

We now calculate the sum J_2 of terms in (10) with $i \approx i_m$. Using the formula for ε_i when $i \gg 1$ from (4) and the Stirling formula, replacing summation by integration in accordance with the usual rules, and evaluating the obtained integral by the Laplace method [10], we have $[f_m = f(i_m)]$

$$J_2 \approx i_m (1+\beta i_m f''_m)^{-1/2} \exp\{\alpha i_m - \beta f_m + i_m(1-\ln i_m)\}. \tag{16}$$

(In [6] an error was made in the calculation of this quantity.)

Substituting (16) into (10) and using formula (13) for α and the asymptotic form $f_m \approx 4i_m^{2/3}$, we write the equation for i_m in the form

$$i_m \left(1 - \frac{8}{9} \frac{\beta}{i_m^{1/3}}\right)^{-1/2} \exp\left\{i_m - \frac{1}{2} - \frac{4}{3} \beta i_m^{2/3}\right\} \approx \frac{\rho}{\rho_a} - J_1, \tag{17}$$

where J_1 is also a function of i_m and β. If (17) for a given ρ/ρ_a and β has a solution i_m satisfying the inequality in (13), aggregation involving the formation of very large aggregates takes place; otherwise, aggregation practically ends at the stage of formation of a particular number of doublets and triplets. It is easy to see that (17) has a solution at large β, provided that $\rho/\rho_a - J_1 > 0$.

It is convenient to introduce a new unknown $\sigma = \beta/i_m^{1/3}$, for which from (17) we obtain the equation

$$\frac{4}{3} \sigma \approx 1 - \frac{\sigma^3}{2\beta^3} - \left(\frac{\sigma}{\beta}\right)^3 \ln\left\{\left(\frac{\rho}{\rho_a} - J_1\right)\left(\frac{\sigma}{\beta}\right)^3 \left(1 - \frac{8}{9}\sigma\right)^{1/2}\right\}, \tag{18}$$

where J_1 is understood as a function of σ and β. The solution of (18) under certain conditions can be represented as follows:

$$\sigma \approx \frac{3}{4} - \left(\frac{9}{16\beta}\right)^2 \left[\frac{1}{2\beta} + \frac{1}{\beta}\left\{\ln\left(\frac{\rho}{\rho_a} - J_1\right) - 3\ln\beta - 1{,}8\right\}\right], \tag{19}$$

and J_1 is estimated when $\sigma = 3/4$. This solution is obviously valid when $|\sigma - (3/4)| \ll \sigma$.

We first assume that $J_1 \ll \rho/\rho_a$. In this case, even when $\rho/\rho_a = 0.01$ and $\beta = 10$ the error of the approximate relation $\sigma \approx 3/4$ is only 3.5%; with increase in ρ/ρ_a and β the error decreases. Hence, the condition for validity of the simple asymptotic formula

$$i_m \approx (4\beta/3)^3 \approx 2.4\beta^3,\ \beta \gg 1, \tag{20}$$

which gives the equilibrium size of the most probable large aggregates in the case of "strong" aggregation, acquires the form

$$\frac{\rho}{\rho_a} - J_1 \gg \exp\left(-\frac{64}{27}\beta^3\right),\ \beta \gg 1. \tag{21}$$

The quantity on the right-hand side of (21) when $\beta \gtrsim 10$ is extremely small and, hence, the curve $\beta = \beta_*(\rho/\rho_a)$, which demarcates the region of strong and weak aggregation on the parametric plane $(\beta, \rho/\rho_a)$, is given by the relation $\rho/\rho_a \approx J_1(\sigma, \beta)$ when $\sigma = 3/4$. When a representative point crosses this curve there is a "phase transition" — in a weakly aggregated system rapid aggregation occurs until the investigated equilibrium state with large aggregates is established.

Unfortunately, the construction of this curve is difficult, since the exact expression for J_1 is unknown. If instead of J_1 we use its upper limit from (14), the corresponding curve is given by the equation [we use (20) here]

$$18\beta^3 \exp\{-\beta + 18\beta^3 \exp(-\beta)\} \approx \rho/\rho_a. \tag{22}$$

At values $\beta = \beta_*$ equal to 10, 12.5, 15, and 17.5, the right-hand side of (22) is equal to 1.82, 0.15, 0.018, and 0.0024, respectively. This phase transition in a system with a given value of ρ/ρ_a becomes possible in principle when $\beta > \beta_*$, and from the condition $\rho/\rho_a < 1$ we obtain the minimum value of β_* (≈ 11.5).

If we use as J_1 its lower limit from (14), then values of β_* slightly smaller than those calculated from (22) will correspond to the former ρ/ρ_a.

At a distance from the phase equilibrium curve in the parametric plane in the region of strong aggregation, formulas (13) for α and (20) for i_m are approximately valid, which determines the equilibrium state of the system, including the numbers ν_i calculated in (9). Using again the Laplace method of asymptotic evaluation of integrals [10], we can easily obtain expressions for the thermodynamic potentials introduced above, and then we can use a standard method to determine the amount of heat evolved by the system during aggregation, and so on. In view of limited space these results, whose obtainment is trivial, are not given here.

Model System. The variance of the distribution of the number of large aggregates with respect to the number of particles contained in them is proportional, as is easy to show, to $\beta^{-3} \ll 1$. At the same time, the number of doublets and other small aggregates in a suspension in which large aggregates are suspended is small in comparison with the singlet content. Hence, when $\beta \gg 1$ we can consider a simplified model of a real, strongly aggregated system composed of only singlets and identical large aggregates in which the number of particles is given by formula (20). The only unknown parameter in this model is obviously the total number of singlets ν_1 (or their fraction $n_1 = \nu_1/N$). Performing calculations similar to those above we obtain the following relations in place of (1), (3), and (6):

$$W = \frac{M!}{(M-N)!\,(i_m!)^{\nu_m}\nu_1!\,\nu_m!\,M^{\nu_m(i_m-1)}}, \tag{23}$$

$$U = -\varepsilon' N + \varepsilon'\nu_1 + \varepsilon f_m \nu_m = \left(-\varepsilon' + \frac{\varepsilon f_m}{i_m}\right)(N - \nu_1), \tag{24}$$

$$S = S_0 + Nk\left\{-n_1 \ln n_1 + n_m \ln\left(\frac{1}{i_m}\frac{\rho}{\rho_a}\right)\right\}, \tag{25}$$

where S_0, as before, is given by the formula in (6), and the free energy F has the form of (7).

Minimizing the free energy with respect to the parameter ν_1 we obtain

$$n_1 = \frac{\nu_1}{N} = i_m \frac{\rho_a}{\rho} \exp\left(-\beta' - 1 + \beta\frac{f_m}{i_m}\right) \approx 18\frac{\rho_a}{\rho}\beta^3 \exp(-\beta'), \tag{26}$$

which also gives the quantity $\nu_m = (N - \nu_1)/i_m$ [the approximate equality is obtained by the use of formulas (20) and $f_m \approx 4i_m^{2/3}$].

Formula (26) is as accurate as the formula for the number of singlets, obtained from (9) with the aid of (4), (13), and (20).

Instead of expressions (8) for the chemical potentials we have

$$\begin{gathered} \mu_1 = \mu_0 + kT \ln n_1, \\ \mu_m = \mu_0 - \varepsilon' + \varepsilon\frac{f_m}{i_m} - kT\left\{1 + \ln\left(\frac{1}{i_m}\frac{\rho}{\rho_a}\right)\right\}. \end{gathered} \tag{27}$$

The condition for equilibrium of the system is the equality of the chemical potentials of the singlets and particles contained in the aggregates. Using (26) it is easy to verify that this condition is fulfilled identically.

The obtained expressions are relatively simple and correctly represent the properties of a strongly aggregated dispersion. Hence, it is convenient to use them in investigations of the diverse physical properties of such a dispersion. We give two examples.

From (26) and (27) we obtain a simple formula for the amount of heat Q released during aggregation:

$$Q = N(\mu_0 - \mu_1) = -NkT \ln n_1 \approx NkT \{\beta' - 3\ln\beta + \ln(\rho/\rho_a) - 2{,}9\}. \qquad (28)$$

It is clear that this result can be of practical value in experimental investigations. For instance, by measuring Q we can draw some inferences regarding the concentration of aggregates in the system or the particle binding energy.

The second example relates to the application of the obtained results to the investigation of significantly nonequilibrium processes in dispersions. In [11] a formal analogy was established between a diffusive Brownian flow of particles or aggregates in a dispersion and a convective flow under the action of thermodynamic forces proportional to the gradients of the corresponding chemical potentials. In particular, the following expression was obtained in [11] for the coefficient of Brownian diffusion in constrained conditions for a suspension of single particles:

$$D = \frac{K(\rho)}{6\pi\eta a}\,\frac{\rho}{1-\rho}\left(\frac{\partial\mu_1}{\partial\rho}\right)_{T,p}. \qquad (29)$$

For a dilute system $K \approx 1 - 6.55\rho$, and μ_1 can be evaluated, for instance, by using the virial expansion for a slightly nonideal gas [9], as was done in [11].

It is obvious that the results of this study, leading to simple relations for the chemical potentials, can be used to extend the results of [11], firstly, to a suspension of moderate concentration (the function K(ρ) for such suspensions was calculated in [12]) and, secondly, to suspensions with appreciable aggregation.

NOTATION

a, particle radius; E_i, energy of aggregate of i particles; F, free energy; f(i), number of particles on surface of large aggregate; i, number of particles in aggregate; J, J_1, and J_2, sum in (10) and its components; K(ρ), function in (29) taking account of constraint effects; k, Boltzmann constant; l, minimum distance between surfaces of particle in aggregate; M, number of cells in lattice; N, total number of particles; $N_i = i\nu_i$; $n_i = N_i/N$; R_i, radius of large aggregate; r, quantity defined in (12); Q, heat released by aggregation; S, entropy; T, temperature; U, internal energy; V, volume of system; v, volume of particle; W, number of states of system; Z, statistical sum; z', z", number of interparticulate bonds per particle within and on surface of large aggregate; α, activity; $\beta = \varepsilon/kT$; $\varepsilon = (z' - z'')\Delta\varepsilon$; $\varepsilon' = z'\Delta\varepsilon$; Δε, half of binding energy of two interacting particles; ε_i, surface defect of particles in aggregate of i particles; η, viscosity of liquid; μ, chemical potential; ν_i, total number of aggregates composed of i particles; ρ, ρ_a, volume concentration of particles in system and within aggregates; $\sigma = \beta/i_m^{1/3}$. Subscripts: m, most probable aggregates; i, aggregates composed of i particles; asterisk, critical values of parameters.

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EFFECT OF IRRADIATION ON DENSITY OF POLYMERS

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A survey is made of available data on the effect of irradiation on the density of several polymers. Results of measurements are presented pertaining to the density of polyethylene, polystyrene, polymethyl methacrylate, and polytetrafluoroethylene at temperatures from −196 to +100°C.

The few available published data on the density of irradiated polymers pertain to the temperature range of +20°C and higher. It seems appropriate to separate the data pertaining to crystalline substances from those pertaining to amorphous ones, inasmuch as irradiation affects them through different mechanisms.

In crystalline polymers (polyethylene, polypropylene, polytetrafluoroethylene, etc.) the change of density is related to amorphization (or with increasing crystallinity, as in the case of polytetrafluoroethylene, with fragments of molecules aligning together and forming small crystals during the process of radiative decomposition) and to cross-linkage of polymer chains occurring principally in the amorphous phase. The change of density in amorphous polymers (polystyrene, polymethyl methacrylate, etc.) is determined by the competing processes of radiative linkage and decomposition. Amorphization of polymers lowers their density, since $\rho_c > \rho_a$ (densities of crystalline phase and amorphous phase respectively) over the entire temperature range. As a result of radiative linking, the density of a polymer increases on account of the decreasing free space. Decomposition has, as a rule, the opposite effect.

In many cases radiative macroeffects involving density, viz., those associated with pore and crack formation as a result of gas evolvement during irradiation, must also be taken into account. Such effects depend overridingly on the irradiation temperature and on the power of the absorbed radiation dose.

The data in Fig. 1 represent results of density measurements made for high-density polyethylene at +20°C [1-3]. The parameter here is the irradiation temperature t_0. At relatively low irradiation temperatures t_0 (20-30°C) the amorphization of high-density polyethylene resulting in a decrease of density is largely compensated by radiative linking. Consequently, the density either hardly changes or slightly increases over a wide range of absorbed radiation doses. As the irradiation temperature t_0 is raised, the amorphization of high-density polyethylene accelerates rapidly [4] while the radiative-chemical linkage yield changes little. Accordingly, the density of high-pressure polyethylene decreases until the radiation dose reaches a certain level of the order of D = 5-7 MgR at which the crystallinity level in the polymer is already low (reduced from 50 to 5-7% at t_0 = 80°C and measured at t_m = 20°C) and then increases as a result of further linking. Measurements of HPPE (high-pressure polyethylene) density ρ at temperatures t_m up to 80°C, not published in report [1], have revealed that the trend of the $\rho = f(D)$ curves remains the same as in Fig.

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