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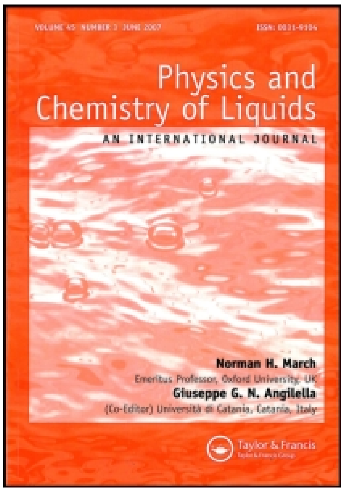

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Structure of Liquid Sulfur Through Polymer Percus-Yevick Theory

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STRUCTURE OF LIQUID SULFUR THROUGH POLYMER PERCUS-YEVICK THEORY

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The static structure factor $S(k)$ for liquid sulfur is calculated via an analytical solution of the Polymer Percus-Yevick (PPY) equation using the fused hard sphere polyatomic model. As the first step in this direction we have applied the ideal chain approximation in which formation of ring polymers is neglected. The chain molecule is represented to be formed by hard sphere beads with two independent attractive sites displaced inside the hard core. The beads adjucent within a given chain penetrate each other at a distance L between their centres. Theoretical results are comparted with experimental data. The theory gives the correct qualitative form for the small and large wavelength region of structure factor. The analysis of the $S(k \rightarrow 0)$ limit is presented also.

Keywords: Integral equations; structure factor; polymer chains

1. INTRODUCTION

The investigation of the equilibrium behaviour of elemental sulphur is of a problem that has received a good deal of attention. This is due in part to the importance of these macromolecules in the chemical industry.

Sulphur is belived to consist of S_8-rings as structural units with an average bond length and angle of 2.05 Å and 108°, respectively [1]. It melts at about 115°C and forms a light yellow liquid of relatively low

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viscosity. Arround a temperature $T_p = 160°C$ the viscosity of liquid sulphur rises drastically. Also other its physical properties such as the density, thermal expansion, refractive index and specific heat show characteristic anomalies [1–4]. Critical phenomenon in sulphur is commonly explained by the S_8-ring breaking off and the S_m-chain forming. Evidence for polymer formation in the system is derived mainly from viscosity [5] and thermal measurements [6]. But direct spectroscopy evidence for the formation of long polymer is minimal [7] and the true composition of the liquid is a matter of conjecture. For example, species varying from S_2 to S_8 have been observed in the saturated vapor phase [8]. Thus, one can suppose that above the transition point the long chains decompose with increasing temperature and form smaller molecules.

In connection with this it is important to investigate the structure within the wide temperature range including the transition point. This has been performed by means of neutron [9–12] and x-ray scattering [13]. There have been several attempts to model liquid sulfur [14–16]. Experimental data have been compared refs. 9 and 10 with the S_8 model of Stillinger *et al.* [17] and the model of Popescu [16] for packed polymer sulfur chains and rings. These models are not tractable analytically and, besides, they do not agree satisfactorily with the experimental shapes for different temperatures.

In the present investigation we apply PPY theory to study the structure of liquid polymer sulfur using a fused hard sphere (FHS) polyatomic model. We will focus only on freely jointed chain version of the model.

The analysis of experimental study of liquid sulphur requires one to take into account the existence of an inherent chain-ring polydispersity. As the first step of our theoretical investigation in this direction we assume the negligible influence of rings on the structure of the system in hand, although, the polyatomic model, which we present in this work, could describe such polydispersity.

2. THEORETICAL PROCEDURE

Our model consists of hard sphere of diameter $D = 1$, which in addition to the hard core interparticle interaction involves the intracore square-well attractive interaction. The total interparticle pair potential is given by

$$U(12) = U_R(r) + U_{AB}(12) + U_{BA}(12) \tag{1}$$

where 1 and 2 denote the positions $\mathbf{r}_1$, $\mathbf{r}_2$ and orientations Ω_1, Ω_2 of two particles with two off center attractive sites A and $B, r = | \mathbf{r}_1 - \mathbf{r}_2 |$. The repulsive part $U_R(r)$ is

$$U_R(r) = \begin{cases} \infty, & \text{for} \quad r < L \\ D_0, & \text{for} \quad L < r < 1, \quad (D_0 > 0) \\ 0, & \text{for} \quad r > 1 \end{cases} \tag{2}$$

while the attractive parts $U_{AB}(12)$, $U_{BA}(12)$ are mediated by the sites A and B, which belong to different monomers

$$U_{GG'}(x) = \begin{cases} -\Phi_0[1 - \delta_{GG'}], & \text{for} \quad z < \Delta, \quad (\Phi_0 > 0) \\ 0, \quad \text{for} \quad z > \Delta \end{cases} \tag{3}$$

Here G denotes A or B and G' denotes its complementary site; GG' denotes AB or BA; z is the distance between sites A,B. Parameter L is the distance between the centers of adjucent monomers which form the macromolecule and Δ is the value that geometrically guarantees the only one bond per site [20]. It is assumed that positions of the two sites A and B, which belong to the same monomer, are independent [19] and randomly distributed at the same distance from the sphere center.

To provide analytical treatment of the present model we consider it in the sticky point limit [21], which can be achieved by letting first $\Delta \to 0, \Phi_0 \to \infty$ and then taking $D_0 \to \infty$, under the constraint that the second virial coefficient for the association potential is kept constant. In this limit the associative part of the potential has been substituted by the Dirac delta-function, so that $\bar{F}_0(r) \to K_0 \, \delta(r - L)/(4\pi L^2)$. Here $\bar{F}_0(r)$ is an orientation-average of $F_0(x) = e_R(r) f_0(x)$, where $e_R(r) = \exp[-\beta U_R(r)], f_0(x) = \exp[-\beta U_{GG'}(x)] - 1$ and $\beta = 1/k_B T$. K_0 is the parameter for the strength of association. Thus, one can see that the theory is independent of the sites displacement and on the angular limit of their bonding, if described in terms of K_0 parameter. It is worth noting that such an approximation eliminates any temperature dependence since the direct connection with the square well potential (3) is broken. In order to recover the temperature dependence we should interrelate the values K_0 with the square well parameters Φ_0 of the initial potential. Within the second virial coefficient approximation the relationship required is given by

$$K_0 = \lambda[\exp\{\beta\Phi_0\} - 1] = \lambda[\exp\left\{\frac{1}{T^*}\right\} - 1]. \tag{4}$$

The value $T^* = (\beta\Phi_0)^{-1}$ is the dimensionless measure of temperature. The constant λ arises after the averaging over orientations. This value depends on the displacement of the sites inside the molecule and also on the angular limit for the site-site bonding. We, therefore, conclude that the temperature properties of a polyatomic system with arbitrary geometry of the site displacement could be recovered through the above scheme, but with the precision of the second virial coefficient. So as not restricted to any particular choice for λ, the latter has been set equal 1. For the purpose of recovering the temperature T corresponding to any λ one has to use the following rescaling formula

$$T = \ln\left[1 + \frac{\exp(T^*) - 1}{\lambda}\right]$$

Due to the randomness in the positions of G,G' sites our polyatomic model presented above can form chain and ring structures. To simplify the analytical solution of the corresponding integral equation we are utilizing here the so-called ideal chain approximation (ICA) [18, 19] in which formation of the ring polymers is neglected. The conformation of chain molecules is not specified at the beginning, rather it is determined as an outcome of the physical association between monomers. Chain formation occurs due to strong attractive forces between the attraction sites, and the structure of chain molecules is a result of these attractions in addition to the usual repulsion between monomers.

The multidensity integral equation formalism for the model in question has been developed in Ref. [20]. Therefore we shall omit any details of the diagrammatical analysis and report here the major results only. Similiar as in Ref. [19] we consider an orientationally-averaged version of the theory, although there is an angle dependence of covalent bonding in sulfur. The anisotropy of the attraction is described through the steric saturation conditions. The correlation functions for associating particles with independent attraction sites can be angle averaged independently over orientation of the each attraction site, and an angle averaged version of the four-density Ornstein-Zernike-like matrix equation for the present model has the following form:

$$\mathbf{h}(r) = \mathbf{c}(r) + \int \mathbf{c}(s)\boldsymbol{\sigma}\mathbf{h}(|\,\mathbf{r} - \mathbf{s}\,|)ds \tag{5}$$

where the partial pair and direct correlation functions, $h_{ij}(r)$ and $c_{ij}(r)$ are the elements of the symmetric matrix $\mathbf{t}(=\mathbf{h}$ or $\mathbf{c})$

$$\mathbf{t} = \begin{pmatrix} t_{00} & t_{0A} & t_{0B} & t_{0\Gamma} \\ t_{A0} & t_{AA} & t_{AB} & t_{A\Gamma} \\ t_{B0} & t_{BA} & t_{BB} & t_{B\Gamma} \\ t_{\Gamma 0} & t_{\Gamma A} & t_{\Gamma B} & t_{\Gamma\Gamma} \end{pmatrix}$$

The lower indices i (or j) in partial correlation functions denote the unbonded ($i=0$), singly bonded ($i=G$) and doubly bonded ($i=\Gamma$) states of the correspondent sulfur atom. The $\boldsymbol{\sigma}$ matrix in (5) is given by [19, 20]

$$\boldsymbol{\sigma} = \begin{pmatrix} \sigma_\Gamma & \sigma_B & \sigma_A & \sigma_0 \\ \sigma_B & 0 & \sigma_0 & 0 \\ \sigma_A & \sigma_0 & 0 & 0 \\ \sigma_0 & 0 & 0 & 0 \end{pmatrix} = \rho \times \begin{pmatrix} 1 & 1/m & 1/m & 1/m^2 \\ 1/m & 0 & 1/m^2 & 0 \\ 1/m & 1/m^2 & 0 & 0 \\ 1/m^2 & 0 & 0 & 0 \end{pmatrix}$$

Here ρ is the monomer density and m is the parameter which can be treated as the mean chain length (within the ICA). This length depends on the stickiness (or temperature), density and bond length L [20]

$$m = \frac{\sigma_\Gamma}{\sigma_G} = \frac{\sigma_G}{\sigma_0} = 1 + \sigma_G K_0 y_{00}(L) \tag{6}$$

where $y_{ij}(r)$ are the analogues of the cavity correlation functions and the value $y_{00}(L)$ can be calculated due to (A7). Eqs. (6) and (4) allow us to derive

$$T^* = \frac{1}{\ln[(m^2 - m)/(\rho y_{00}(L)) + 1]} \tag{7}$$

The dependence $T^* = T^*(m,\eta)$ is shown in Figure 1. As is seen, the formation of long chains is preferable at low temperature and high packing fraction $\eta, \eta = \pi\rho D^3/6$. With increasing temperature, starting from $T^* \approx 0.7$, the chains become to decompose.

In this study we are using the PPY closure conditions which with the ICA for the present model reads [19, 20]

$$h_{ij}(r) = -\delta_{i0}\delta_{jo} + \frac{Me_R(r)}{L}\delta(r-L)\delta_{ij}^{[1,2]}, \quad \text{for} \quad r \leq 1 \tag{8}$$

$$c_{ij}(r) = 0, \quad \text{for} \quad r > 1 \tag{9}$$

where we have used the notation $M = m(m-1)/(4\pi\rho L)$ and $\delta_{ij}^{[1,2]} = \delta_{i1}\delta_{j2} + \delta_{i2}\delta_{j1}$.

The OZ equation (5) together with the PPY closure conditions (8) and (9) form a closed set of equations to be solved. Since all direct correlation functions are finite-ranged, the factorized version of eq.(5) can be obtained applying the Baxter factorization technique [22]:

$$rh_{ij}(r) = -q'_{ij}(r) + 12\sum_{nk}\int_0^1 q_{in}(t)\eta_{nk}h_{kj}(|\, r-t \,|)(r-t)dt \tag{10}$$

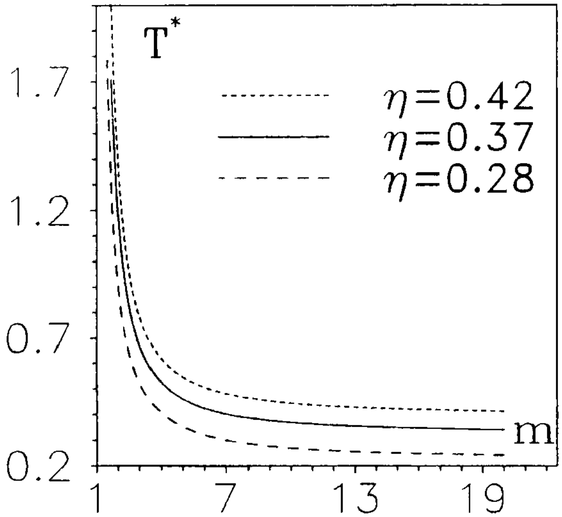

FIGURE 1 Mean chain length m as function of reduced temperature T^* at different packing fractions.

$$rc_{ij}(r) = -q'_{ij}(r) + 12\sum_{nk}\frac{\partial}{\partial r}\left(\int_0^{1-r} q_{ni}(r)\eta_{nk}q_{kj}(r+t)dt\right) \tag{11}$$

where $\boldsymbol{\eta} = \pi\boldsymbol{\sigma}/6$ and $q_{ij}(r)$ are the auxiliary factor q-functions, $q_{ij}(r) = 0$ for $r > 1$ and $r < 0$. The boundary conditions (8) on $h_{ij}(r)$ is substituted into eq. (10) to determine $q_{ij}(r)$ on the range $0 < r < 1$. It yields the differential-difference equations for $q_{ij}(r)$

$$\begin{aligned} q'_{ij}(r) = \delta_{j0}(a_i r + b_i) + 12\sum_{mk}\eta_{km}\delta_{mj}^{[1,2]}M[q_{ik}(r-L) \\ - q_{ik}(r+L)] - M\delta(r-L)\delta_{ij}^{[1,2]}, \end{aligned} \tag{12}$$

where

$$a_i = \delta_{i0} - 12\sum_{k=0}^{3}\eta_{k0}\int_0^1 q_{ik}(t)dt, \quad b_i = 12\sum_{k=0}^{3}\eta_{k0}\int_0^1 q_{ik}(t)t\mathrm{d}t, \tag{13}$$

The technical details of solving (12) are given in Ref. [20]. We simply note here that it is necessary to divide the interval [0,1] into three domains [0,1−L], [1−L, L), (L, 1] and convert the differential difference equations connecting the $q_{ij}(r)$ on each domain into a set of ordinary linear equations with constant coefficients. The procedure for their recovering is briefly discussed in Appendix.

Knowledge of q-functions enables one to calculate the structure factor (SF) $S(k)$ for our model due to the relation [20]

$$S(k) = \frac{1}{\rho}\{[\mathbf{q}(k)\boldsymbol{\sigma}\mathbf{q}^T(-k)]^{-1}\}_{00}, \tag{14}$$

where the elements of matrix **q**(k) are defined by the relation

$$\hat{q}_{ij}(k) = [\boldsymbol{\sigma}^{-1}]_{ij} - 2\pi\int_0^1 q_{ij}(r)\exp(ik)dr \tag{15}$$

and reported in Ref. [20].

3. RESULTS AND DISCUSSION

The detail studing of the peculiarities of theoretical structure factor, $S_t(k)$, for the model considered has been recently presented [20].

Namely, it is shown, that the overlapping of chain beads increases the magnitude of the pre-peak, which appears at small wavenumbers ($k_p \approx 3$) even at $L=1$. At $L=0.7$ its value is nearly equal to the value of the first peak. It has been found, taht distance between the pre-peak and the first peak increases with decreasing of L.

Among others publications, the experimentally determined structure factor $S_e(k)$ for liquid sulfur at different temperatures has been represented in Ref. [11] by Bellisent *et al.* They have performed a diffraction measurement using hot source neutrons. Here we use the data and general conclusions which have been done in Ref. [11]. Namely, it is assumed that bond length exhibits in the liquid state of sulfur almost the same value as in the crystal, which is very consistent with the strength of sulfur covalent bonding. That is why, to fit the experimental SF we fix here the bond length equal $\tilde{L}=2.05\AA$. (Hereafter, we will use the letters with tilde in order to mark the dimensionful values of correspondent dimensionless parameters). Since the sample which has been investigated [11], consisted of 3.5 cm^3 (about 6g) of 99.999% purity sulfur, we fix also the number density $\tilde{\rho} = 1.7g/cm^3$.

It is well known that the value of "hard-sphere" core diameter of monomer particle $\tilde{D}$ depends on the temperature of the system [23]. Therefore, the packing fraction of FHS-polyatomic model is the function of temperature too. Figure 2 depicts the experimentl SF [11] and its theoretical fitting for a system of sulfur atoms at $T = 200°C$(a) and $T = 300°C$(b). At lower temperature we use the model chains with averaged length $m=25$ and packing fractions $\eta=0.34$, which corresponds to $\tilde{D}=2.73\AA$. At higher temperature the mean chain length is equal to 16 and $\eta=0.32$ ($\tilde{D}=2.68\AA$). The decreasing of mean chain length with the temperature is a physically evident fact, since the thermal motion broke not only S_8-rings but long chains also.

In general, the fit to the data is quantitatively superior to that obtained in Ref. [10]. But, at $\tilde{k} \approx 7\AA^{-1} \pm 1\AA^{-1}$, our model, within the ICA, is seen to be in rather poor agreement with experimental data. However, this is to be expected, since we deal with randomly located sites, whereas sulfur is known to have a certain angle between the bonds. Besides, we do not try to fit the shoulder at $\tilde{k} \approx 1.25\AA^{-1}$. Concerning the experimental results [9–12], this shoulder broadens and almost collapses into the pre-peak when temperature increases.

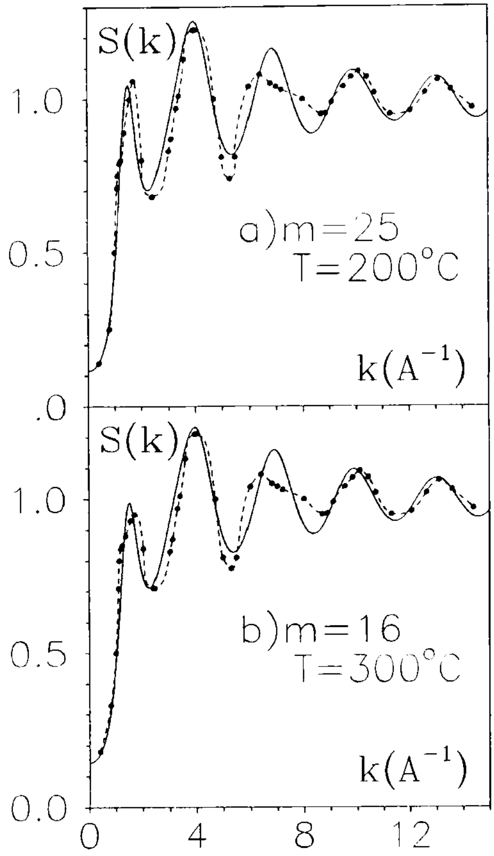

FIGURE 2 The experimental structure factors (dashed curve with points) at T = 200°C (a); T = 300°C (b) [11] and the fitting theoretical ones (solid line) for $m = 25(a)$; $m = 16(b)$. The packing fractions are $\eta = 0.34$ (a) and $\eta = 0.32$(b).

Thus, one can explain this feature of SF by the S_8-rings influence, which is weakenes with temperature. We expect to obtain such shoulder after using more precise solution of PPY, which takes into account the ring-chain polydispersity.

To make more clear the fitting process, the theoretical SF is plotted in Figure 3 where we display the changes in $S_t(k)$ caused by increasing packing fraction η and association K_0 (or mean chain length m). It is seen that the curves differ mainly in small $\tilde{k}$ region. This means that association effects induce the intermediate-range correlation, but very

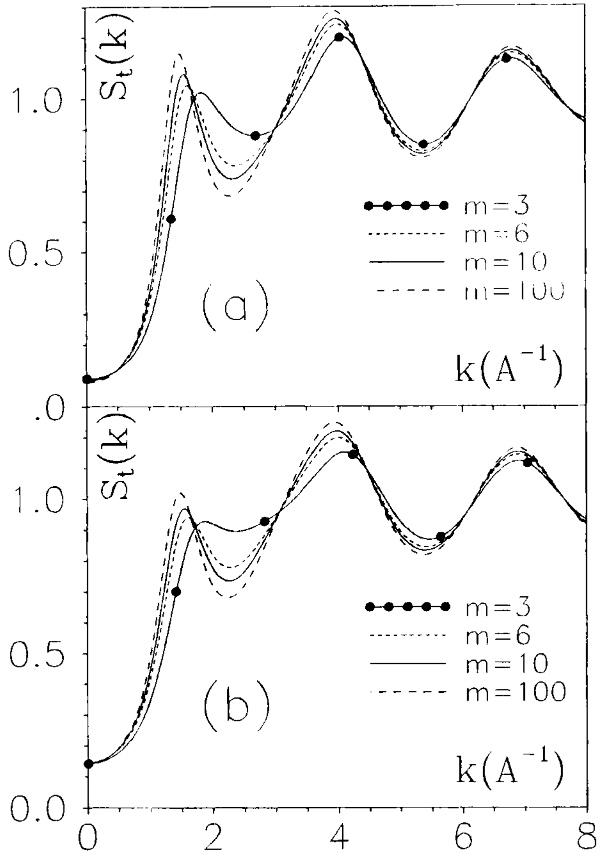

FIGURE 3 The theoretical structure factors $S_t(\tilde{k})$ for different values of mean chain lengthes. The packing fractions are $\eta = 0.36$(a) and $\eta = 0.32$(b)

short range order is not sufficiently changed with m and η. Such behavior of theoretical SF is similiar to those detected in the experiments [10–12].

The genesis of the pre-peak at $1 < \tilde{k}_p < 2$ can be seen also from Figure 3. To illustrate the temperature dependence of the theoretical SF we show in Figure 4 the dependence of the pre-peaks magnitude $S_1 = S(k_p)$ on the association and packing fraction. As is seen, after sharp decreasing, the pre-peak becomes higher with increasing of mean chain length as well as with increasing of packing fraction. This

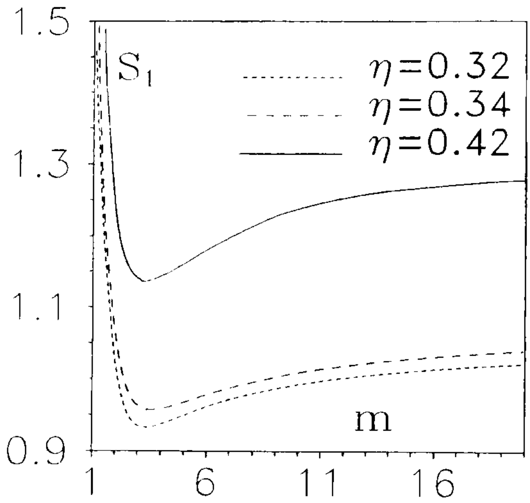

FIGURE 4 Magnitude $S_1 = S(\tilde{k}_p)$ of the pre-peak as functions of mean chain length for the different packing fractions.

can be interpreted as increasing of the connectedness of sulfur atoms due to association. Pre-peak regenerates in the first peak with large magnitude at small *m* (or high T^*) region. Based on this, one can expect, that experimental investigations of liquid sulfur at higher temperature (at least, more than 350°C) would determine such effect.

From the full expression for $S(k)$ its low k limit can be expressed. $S(0)$ is an important quantity because it is connected with the isothermal compressibility by

$$S(0) = \rho k_B T \chi_T$$

Therefore, the behaviour of $S(0)$ is closely related to the compressibility pressure equation and to the phase diagram of the system. In order to obtain $S(0)$ it is necessary to have the $\hat{q}_{ij}(0)$, which readily folows from equation (15) [20]. The value $S_t(0)$ as a function of *m* at different η is plotted in Figure 5. As mentioned above, it should be kept in mind that packing fraction depends on temperature as well as mean chain length does. If one of these parameters is fixed, we could obtain the tendensy of $S_t(0)$ behaviour, which is analogous to those detected in the experiments [11, 12]: the compressibility decreases with decreasing of temperature.

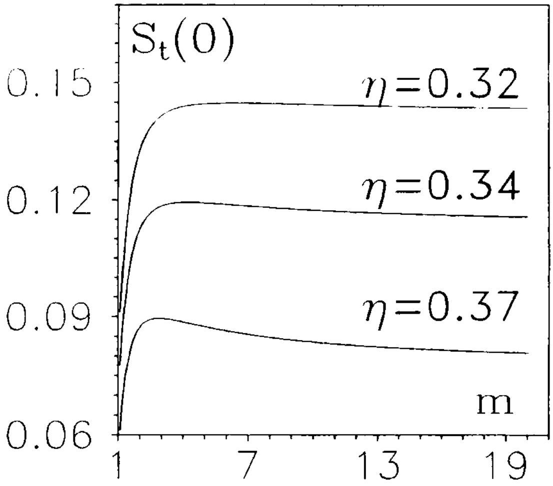

FIGURE 5 The theoretical structure factor $S_t(k \to 0)$ as function of mean chain length for the different packing fractions.

To estimate the real values of "theoretical" temperatures one should use eq. (4) and know the magnitude of associative potential Φ_0. But this problem is out of scope of work presented.

4. CONCLUSIONS

After applying Wertheims multidensity formalism to the consideration of the fused hard sphere polyatomic model, the structure of liquid sulfur has been investigated. It has been shown that this primitive model can be used, in principle, for the description of liquid sulfur in a wide range of temperature above the critical temperature of polymerization. The results clearly demonstrate that liquid sulfur structure is strongly affected by the length of polymer chains. Since this length depends on the temperature, temperature dependence of structure properties is a function of mean chain length as well as a function of "hard core" diameter.

There are, of course, a number of limitations to the present theoretical results. An improvement in this polymer model would consist in considering the angle dependence of associative bonding. In the near future we plan to study the experimentally determined temperature dependence of liquid sulfur properties in wider temperature intervals due to the ring-chain polydisperse version of this model.

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5. APPENDIX

a) The factor q-functions are defined as

$$q_{i0}(r) = \frac{1}{2}a_i(r^2 - 1) + b_i(r - 1) \quad \text{and } q_{i3}(r) = 0 \qquad \text{(A1)}$$

In the case of $j \neq 0$ and $j \neq 3$ these functions have the following form:

$$q_{ij}(r) = m\left\{\left[-\frac{1}{2}a_i\right]r^2 + \left[-\frac{a_i}{\omega} - b_i\right]r + \frac{1}{\omega^2}\left[a_i - \omega(a_iL + b_i) + \omega^2\left(\frac{1}{2}a_i + b_i\right)\right] + u_{ij}\cos(\omega r) + v_{ij}\sin(\omega r)\right\} \quad \text{when} \quad 0 < r < 1 - L; \tag{A2}$$

$$q_{ij}(r) = c_{ij}, \quad \text{when} \quad 1 - L < r < L \tag{A3}$$

$$q_{ij}(r) = m\left\{\left[-\frac{1}{2}a_i\right]r^2 + \left[\frac{a_i}{\omega} - b_i\right]r + \frac{1}{\omega^2}\left[a_i - \omega(a_iL - b_i) + \omega^2\left(\frac{1}{2}a_i + b_i\right)\right] + u_{ij}\sin(\omega(r - L)) - v_{ij}\cos(\omega(r - L))\right\}, \quad \text{when} \quad L < r < 1; \tag{A4}$$

where $\omega = (m - 1)/(2mL)$. Coefficients $c_{ij}, u_{ij}, v_{ij}, a_i$ and b_i should be obtained by solving the following set of therty two linear equations

$$A_z a_i + B_z b_i + C_z \sum_{k=1}^{2} c_{ik}\eta_{k0} + U_z \sum_{k=1}^{2} u_{ik}\eta_{k0} + V_z \sum_{k=1}^{2} v_{ik}\eta_{k0} = R_z, \quad \text{for} \quad z = 1, 2 \tag{A5}$$

$$A_z a_i + B_z b_i + C_z c_{ij} + U_z u_{ij} + V_z v_{ij} = R_z, \quad \text{for} \quad z = 3, 4, 5 \tag{A6}$$

The nonzero constants $A_z, B_z, C_z, U_z, V_z, R_z$ of equations (A5) and (A6) are

$$A_1 = \frac{1}{12} + 2\eta\left[\frac{L^3}{3} - \frac{L^2}{2} - \frac{L}{2} + \frac{1}{2} + \frac{2}{\omega^2}(1 - L) + \frac{1}{\omega}(L - 1)L\right];$$

$$A_2 = \eta\left[\frac{L^3}{2} - \frac{3L^2}{4} + \frac{3}{16} + \frac{1}{\omega^2}(1 - L)\right];$$

$$A_3 = m\left[\frac{1 - L}{\omega} + \frac{1}{\omega^2}\right]; \quad A_4 = m\left[\frac{1 - L^2}{2} + \frac{1}{\omega^2}\right];$$

$$A_5 = m\left[\frac{2L - L^2}{2} - \frac{1}{\omega} + \frac{1}{\omega^2}\right];$$

$$B_1 = \eta\left(\frac{3}{2} - 2L\right); \quad B_2 = -\frac{1}{12} + \eta\left[\frac{2L^3}{3} - L^2 + \frac{1}{4} + \frac{(1-L)L}{\omega}\right];$$

$$B_3 = \frac{m}{\omega}; \quad B_4 = m\left[1 - L + \frac{1}{\omega}\right]; \quad B_5 = m\left[L - \frac{1}{\omega}\right];$$

$$C_1 = 2L - 1; \quad C_2 = L - \frac{1}{2}; \quad C_4 = -1; \quad C_5 = -1;$$

$$U_1 = \frac{1}{\omega}(\sin t - \cos t + 1); \quad U_2 = \frac{1}{\omega^2}(\cos t + \sin t - 1) + \frac{1}{\omega}(L + (1 - L)\sin t - \cos t);$$

$$U_3 = \sin t; \quad U_5 = \cos t;$$

$$V_1 = -\frac{1}{\omega}(\cos t + \sin t - 1); \quad V_2 = \frac{1}{\omega^2}(1 + \sin t - (t+1)\cos t) - \frac{1}{\omega}\sin t;$$

$$V_3 = -\cos t; \quad V_4 = -1; \quad V_5 = \sin t;$$

$$R_1 = \frac{1}{12}\delta_{0i}: \quad R_4 = -(\delta_{i1}\delta_{j2} + \delta_{i2}\delta_{j1})M;$$

Here, $t = \omega(1\text{-}L)$.

b) *Expression for cavity correlation function* follows from the PPY approximations in which (10) and (11) have been used

$$y_{00}(L) = \frac{1}{L}(\xi + b_0) + a_0 \tag{A7}$$

where

$$\xi = -2\pi\sum_{lm}\sigma_{ml}\left\{\frac{1}{8}a_m a_l(1-L)^4 + \frac{1}{3}\left[\frac{1}{2}a_m(a_l L + b_l) + a_l b_m\right](1-L)^3 + \frac{1}{2}\left[b_m(b_l + a_l L) - \left(\frac{1}{2}a_m + b_m\right)a_l\right](1-L)^2 - \left(\frac{1}{2}a_m + b_m\right)(a_l L + b_l)(1-L)\right\} \tag{A8}$$