Evaluation of the compressional compliance of a polymer melt from dynamic light scattering data using linear viscoelastic relations

G. Meier, J.-U. Hagenah, C. H. Wang*, G. Fytas† and E. W. Fischer
Max-Planck-Institut für Polymerforschung, Mainz, and Institut für Physikalische Chemie, Universität Mainz, 6500 Mainz, West Germany
(Received 11 September 1986; revised 13 January 1987; accepted 2 March 1987)

The method of determining the compressional (or bulk) compliance by using the dynamic light scattering spectrum arising from density fluctuations has been evaluated. It is also shown by numerical computation for cases where the relaxation function can be described by a single Williams–Watts function that the numerical technique used to compute the retardation spectrum also gives an identical result.

(Keywords: poly(vinyl acetate); photon correlation; bulk compliance; linear viscoelastic functions; inverse Laplace transformation; Kohlrausch–Williams–Watts function)

INTRODUCTION

The investigation of viscoelastic properties of a polymer melt has been a subject of great interest in material science. Several ingenious mechanical techniques have been designed to measure the shear modulus and the shear compliance of a linear viscoelastic medium over a wide dynamic range[1]. However, only very few direct measurements of the compressional modulus and the compressional compliance of a polymer melt have been reported. This is due apparently to great experimental difficulties encountered in the design of the dynamic pressure transducer. In a previous paper[2] we have investigated the feasibility of using the dynamic light scattering technique to measure the compressional (or bulk) modulus and compressional (or bulk) compliance. Experimental verification using the light scattering data of poly(vinyl acetate) (PVAc) as an example was then carried out[3].

However, two approximations were used in carrying out the comparison between the mechanical compressional data of McKinney and Belcher[4] and the dynamic light scattering data of PVAc[3,5]. First, in order to compute the time-dependent compressional compliance $B(t)$ from the frequency-dependent dynamic compressional compliance, we have used the approximation

$$B(t) \approx [B'(\omega)]_{\omega=1/t} \tag{1}$$

where $B'(\omega)$ is the real part of the dynamic compliance. Having obtained $B(t)$, the Schwarzl–Stavermann approximation[1] given by

$$L(\ln\tau) = \left[\frac{\mathrm{d}B(t)}{\mathrm{d}\ln t} - \frac{\mathrm{d}^2B(t)}{\mathrm{d}(\ln t)^2}\right]_{t=2\tau} \tag{2}$$

was then used to calculate the spectrum of retardation times $L(\ln\tau)$.

These two approximations were consistently employed to treat the dynamic light scattering and mechanical relaxation data. The retardation time spectra obtained from both techniques are shown to agree well in the retardation times ranging from 10^{-3} to 10^{-6} s, but a slight discrepancy is found at times longer than 10^{-3} s. It is not known that the agreement at short times is due to cancellation of errors from the approximations used; neither is it clear about the origin of the disagreement at long times. To clarify these points, we have removed these approximations and used instead a numerical technique to evaluate expressions involving exact linear viscoelastic theory. By doing so, we are also able to evaluate the importance of the shear compliance contribution to the light scattering data of the polymer melt. In dynamic light scattering arising from density fluctuations, one deals strictly with the longitudinal, rather than the compressional, compliance spectrum[2].

COMPUTATION OF THE COMPRESSIONAL COMPLIANCE

As mentioned before, results of direct compressional compliance measurements are rare. Measurements by McKinney and Belcher[4] of the storage and loss compressional compliance B' and B'' of poly(vinyl acetate) (PVAc) are some of the few results available. Here B' and B'' are related to the transient (or time-dependent) compliance $B(t)$ by[1]

$$B'(\omega) = B_e - \omega\int_0^\infty [B_e - B(t)]\sin(\omega t)\,\mathrm{d}t \tag{3}$$

$$B''(\omega) = \omega\int_0^\infty [B_e - B(t)]\cos(\omega t)\,\mathrm{d}t \tag{4}$$

where $B_e = B_0 = \chi_T$, the isothermal compressibility.

---

* Permanent address: Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, USA

† Permanent address: Department of Chemistry, University of Crete, Iraklion, Crete, Greece

0032-3861/87/101640-05$03.00

McKinney and Belcher had measured under adiabatic rather than isothermal conditions $B'(\omega)$ and $B''(\omega)$ of PVAc at various temperatures and pressures and they then applied the temperature–frequency superposition principle and reduced the data to a reference temperature and pressure of 50°C and 1 atm respectively[4]. The reduced $B'(\omega)$ and $B''(\omega)$ data cover more than 12 decades in the frequency domain[4]. The storage compressional compliance B' falls from a low-frequency limiting value B_0 to a high-frequency limiting value B_∞, with a change of more than a factor of 2. On the other hand, the loss compressional modulus B'' vanishes within experimental error at both low and high frequencies and passes through a maximum. The loss tangent is of the order 0.1 and is rather flat. The physical origin of the frequency dependence of $B'(\omega)$ and $B''(\omega)$ is due to the change of free volume involving local configurational adjustments which require a finite time.

Since the loss compressional compliance $B''(\omega)$ involves only a small change, it is more convenient to evaluate $B(t)$ through $B'(\omega)$. Inverting equation (3), we obtain

$$B(t)=\frac{2}{\pi}\int_0^\infty \mathrm{d}\omega\frac{B'(\omega)}{\omega}\sin(\omega t) \tag{5}$$

It is interesting that the equilibrium compliance B_e drops out in the process of integration.

Since $B'(\omega)$ becomes B_0 as $\omega\to0$, and $B'(\omega)$ approaches B_∞ as $\omega\to\infty$, it is useful to define a normalized quantity $A(\omega)$ in accordance with the expression

$$A(\omega)=\frac{B'(\omega)-B_\infty}{B_0-B_\infty} \tag{6}$$

The value of the function $A(\omega)$ is 1 as $\omega\to0$ and 0 as $\omega\to\infty$. It takes on only values between 1 and 0 and is thus convenient for computational purposes. We now express $B'(\omega)$ in terms of $A(\omega)$ and substitute the result into equation (5) to obtain

$$B(t)=B_\infty+(B_0-B_\infty)A(t) \tag{7}$$

where

$$A(t)=\frac{2}{\pi}\int_0^\infty \mathrm{d}\omega\frac{A(\omega)}{\omega}\sin(\omega t) \tag{8}$$

We have calculated $B(t)$ by first computing $A(\omega)$ using the digitized data of $B'(\omega)$ and then numerically calculating $A(t)$ in accordance with equation (8). The result of $B(t)$, constructed from $A(t)$ by using equation (7), is shown in *Figure 1*, in the form of $[B_0-B(t)]/B_\infty$.

Now we recall from the theory of Wang and Fischer[2] that the transient longitudinal compliance $D(t)$ is related to the relaxation function $g(t)$ arising from the density fluctuation which can be measured by the homodyned photon correlation technique according to

$$\alpha_r g(t)=[B_0-B(t)]/B_\infty \tag{9}$$

where α_r is the fraction of scattered light that is detected and processed by the electronic correlator used in the light scattering experiment. The fastest correlator available to date has the sample time of 0.1 μs (corresponding to 1.5 MHz). Thus, dynamic information faster than 1.5 MHz only contributes to the background in the photon correlation experiment.

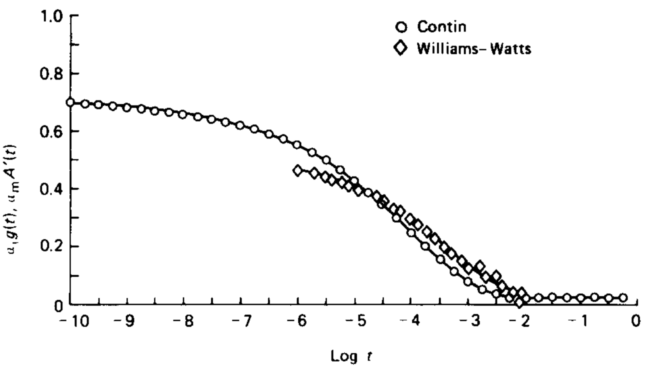

Figure 1 Plot of $\alpha_r g(t)$ (◇) and $\alpha_m A'(t)$ (○) *versus* log t computed from the light scattering data using equation (11) and the mechanical relaxation data using equations (7), (8) and (12) (PVAc, 50°C)

In the actual homodyned photon correlation experiment, one measures under isothermal conditions[5] the autocorrelation function of the scattered light intensity $G(t)$ which is related to $g(t)$, introduced above, by

$$G(t)=A[1+f\alpha_r^2|g^2(t)|^2] \tag{10}$$

where f depends on the size of pinholes and other experimental factors determining spatial coherence. The calibrated value for f is 0.68 for our spectrometer. Thus from equation (10), we find that

$$\alpha_r g(t)=(1/\sqrt{f})\{[G(t)/A]-1\}^{1/2} \tag{11}$$

The $\alpha_r g(t)$ data as determined from the measured $G(t)$ and A at the scattering angle $\theta=90°$ at $T=50°$C for PVAc ($M_n=1.5\times10^4$ and glass transition temperature $T_g=17°$C) are also shown in *Figure 1*. It should be emphasized that no adjustable parameter is used in making the plot. The light scattering data only cover 4.3 decades in time, in contrast to the mechanical data $B(t)$, which encompass more than 12 decades in time because of the use of the temperature–frequency superposition principle. In *Figure 1* the mechanical data are plotted in the form $[B_0-B(t)]/B_\infty$ and no correction for isothermal conditions is needed.

Although the agreement between the light scattering and the mechanical data is satisfactory, discrepancy exists at both sides of the retardation time $t=2.0\times10^{-5}$ s, with the $B(t)$ value being larger at short times and smaller at long times. There are two possible causes for the discrepancy. The main one is that the α_r value (≈0.52)[6] determined in the light scattering experiment is somewhat smaller than the relaxation length associated with the mechanical data. The fraction α_r which is subject to an error of about 10% is probably underestimated due to some elastic light scattering. The mechanical relaxation strength α_m is defined as $\alpha_m=(B_0-B_\infty)/B_\infty$, which is obtained by rewriting equation (7) as

$$B(t)=B_0-B_\infty\alpha_m A'(t) \tag{12}$$

where $A'(t)=1-A(t)$.

The adiabatic B_∞ value can be determined by Brillouin scattering according to $B_\infty = q^2/\rho_m\omega_B^2$, with ω_B being the Brillouin shift measured at the scattering vector $\mathbf{q}$ if B can substitute the longitudinal compliance D as discussed below. Here q is the amplitude of $\mathbf{q}$. The adiabatic B_∞ as determined by Brillouin scattering is $(1.95 \pm 0.08) \times 10^{-11}\ \mathrm{cm^2\,dyn^{-1}}$ for PVAc at 50°C, in contrast to the value of $(2.28 \pm 0.1) \times 10^{-11}\ \mathrm{cm^2\,dyn^{-1}}$, extrapolated from McKinney and Belcher's data obtained using the temperature–frequency superposition principle. This value together with $B_0 = 3.87 \times 10^{-11}\ \mathrm{cm^2\,dyn^{-1}}$ gives $\alpha_m = 0.69$. The smaller B_∞ values gives a larger α_m. The difference between the two is of course associated with the smaller dynamic response associated with photon correlation spectroscopy which is inherently restricted to less than 10 MHz. We could bring the two curves to a better agreement if we set α_r equal to the α_m values, but in order to provide an objective comparison we chose not to do this.

Another possible cause for the discrepancy may be due to the replacement of the longitudinal compliance $D(t)$ by the compressional compliance $B(t)$. We now discuss the error introduced by making this substitution.

For polymer melts, the viscoelastic behaviour in simple extension or in longitudinal deformation will in general combine the features of shear and compressional viscoelasticity; thus, the extensional compliance or the longitudinal compliance depend on both $J(t)$ and $B(t)$, where $J(t)$ is the shear compliance. To discuss the difference between $D(t)$ and $B(t)$, it is more convenient first to consider the relationship[1] among the various dynamic compliances $D^*(\omega)$, $B^*(\omega)$ and $J^*(\omega)$, which are the one-sided Fourier transforms of $D(t)$, $B(t)$ and $J(t)$ respectively:

$$D^* = \frac{B^*J^*}{J^* + \frac{4}{3}B^*} \tag{13}$$

For simplicity we have not explicitly written out the frequency dependence.

Above T_g, the shear dynamic compliance is greater than the compressional compliance by at least one order of magnitude[1]. It is thus appropriate to write equation (13) as a series expansion of B^*/J^*:

$$D^* \simeq B^*[1 - \tfrac{4}{3}(B^*/J^*) + \tfrac{16}{9}(B^*/J^*)^2 + \ldots] \tag{14}$$

The fact that J^* is greater than B^* by at least a factor of 10 shows that the replacement of $D(t)$ by $B(t)$ when handling light scattering data underestimates the value of $B(t)$ by at most 10%. For PVAc[7], the factor B^*/J^* is of the order of 10^{-3}; thus, the error made by replacing $D(t)$ with $B(t)$ in PVAc is inconsequential.

The time dependence of the relaxation function $g(t)$ or $A'(t)$ for polymer melts can usually be fitted to the fractional exponential (or often referred to as the Williams–Watts[8])* function given by $\exp[-(t/\tau_0)^\beta]$, where β is the parameter describing the width of the distribution of the relaxation times, and τ_0 is the intrinsic relaxation time. For PVAc, we have found for the $g(t)$ function from the light scattering data that $\beta = 0.36$ and $\tau_0 = 4.6 \times 10^{-4}$ s, and for the $A'(t)$ function from the mechanical relaxation data that $\beta = 0.35$ and $\tau_0 = 1.1 \times 10^{-4}$ s. Thus, the difference in the two curves as shown in *Figure 1* is also reflected in the different τ_0 values. Possible causes for this difference may be due to a small difference in T_g of the two samples and the large dynamic range that is used to represent the mechanical relaxation data. If the large uncertainty in the mechanical relaxation data ($\approx 20\%$) introduced due to the application of the temperature–time superposition principle were taken into account in the data analysis, the difference in τ_0 would probably not be as large. As shown below, the factor of about 4 in the τ_0 value in the two sets of data will affect subsequent results in the computation.

Despite the apparent success in the use of the fractional exponential function to fit the experimental data, it is more general and also physically more meaningful to analyse the transient compressional compliance $B(t)$ in terms of a continuous spectrum of retardation time L, according to

$$B(t) = B_\infty + \int_{-\infty}^{\infty} L(\ln\tau)(1 - \mathrm{e}^{-t/\tau})\, \mathrm{d}\ln\tau \tag{15}$$

Comparison of (15) with (7) and (12) gives

$$\alpha_m A'(t) = \int_{-\infty}^{\infty} L_l(\ln\tau)\mathrm{e}^{-t/\tau}\, \mathrm{d}\ln\tau \tag{16}$$

where the subscript m indicates the dimensionless mechanical retardation spectrum L.

Similarly for light scattering, we have

$$\alpha_r g(t) = \int_{-\infty}^{\infty} L_l(\ln\tau)\mathrm{e}^{-t/\tau}\, \mathrm{d}\ln\tau \tag{17}$$

where the subscript l indicates light scattering.

Using the computer algorithm developed by Provencher[10] (referred to as Contin version 2), we have numerically inverted the Laplace transform and computed the retardation spectrum $L_m(\ln\tau)$ from the mechanical data shown in *Figure 1*. The result is given in *Figure 2*. To check the accuracy of the 'Contin' program,

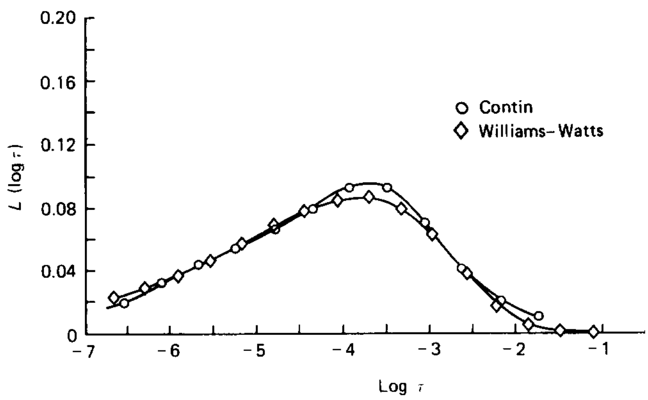

Figure 2 Comparison of the retardation spectrum L_m computed by direct use of the experimental data and the Contin program (○) and the algorithm derived from the Williams–Watts functional fit to the experimental data (◇)

---

* It should be pointed out that this fractional exponential function was already introduced by R. Kohlrausch to describe dielectric relaxation in glasses in 1854, long before Williams and Watts paper in 1971

we have also numerically evaluated the retardation spectra $L_m(\ln\tau)$ and $L_l(\ln\tau)$ derived by using the Williams–Watts representation for $A'(t)$ and $g(t)^{11,12}$. We computed the distribution of retardation times by using

$$L_{l,m}(\ln\tau)=\tau_0\lambda(x,\beta)/\tau \tag{18}$$

where

$$\lambda(x,\beta)=\frac{1}{\pi}\int_0^\infty \exp(-xu)\exp[-u^\beta\cos(\pi\beta)]\sin[u^\beta\sin(\pi\beta)]\mathrm{d}u \tag{19}$$

The latter integral was evaluated numerically. The Williams–Watts result for L_m is also shown in *Figure 2.* Clearly, within the computational uncertainty, there is no deviation between the two results. A further check on the reliability of the Contin program is the back-calculation of the $\alpha_r g(t)$ function using the $L_l(\ln\tau)$ function already calculated using both the Williams–Watts algorithm and the Contin program. Comparison of the results is shown in *Figure 3*. Within the experimental uncertainty, there is no deviation between the two results. Therefore, the Contin program can be used with reliability for computing the retardation spectrum.

Comparison of the two retardation spectra $L_m(\ln\tau)$ and $L_l(\ln\tau)$, calculated by using the Contin program and the mechanical relaxation and light scattering data respectively, is shown in *Figure 4*. One notes that each of the two retardation spectra shows a long tail in the short-time region and also a maximum. The shape of the retardation spectra (L_m and L_l) is similar to the dynamic loss compliance $B''(\omega)$. However, the retardation spectrum L_l shifts consistently to a longer time than the mechanical retardation spectrum L_m mainly due to the slower (by a factor of 4) light scattering time. This result then shows that the agreement of L_m and L_l obtained at short times as reported in ref. 3, using the approximations given by equations (1) and (2), is probably due to cancellation of errors. Discrepancy also exists at long time, but it is not as large as that found in the short-time region.

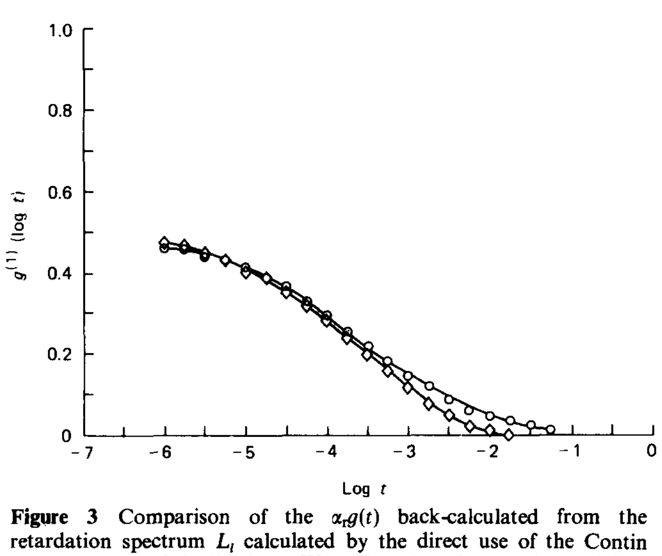

Figure 3 Comparison of the $\alpha_r g(t)$ back-calculated from the retardation spectrum L_l calculated by the direct use of the Contin program (○) and the Williams-Watts fit (◇) to the experimental data (PVAc, 50°C)

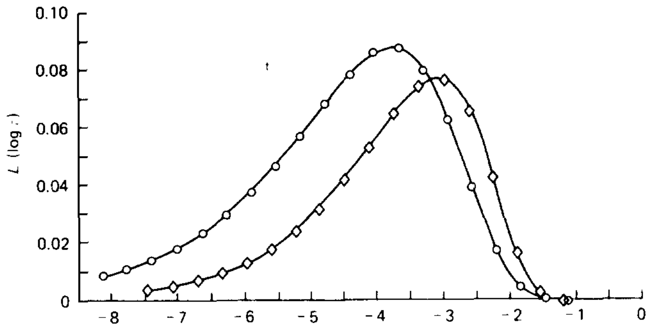

Figure 4 Comparison of the retardation spectra L_m and L_l calculated by using the Contin program from the mechanical (○) and light scattering (◇) data (PVAc, 50°C)

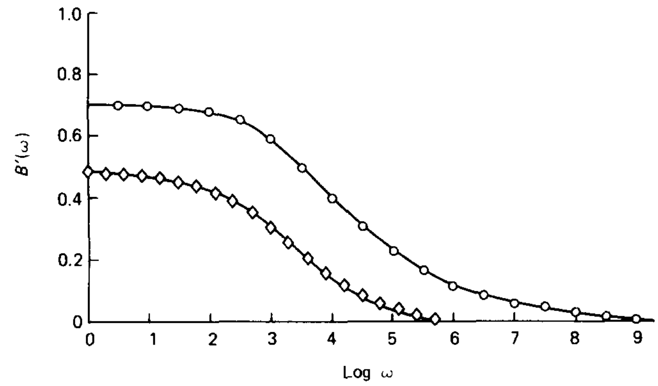

Figure 5 Comparison of the dynamic loss compliance $B'(\omega)$ calculated from the light scattering data (◇) with the mechanical relaxation result (○)

The discrepancy in L_m and L_l will have an effect when they are used to compute other linear viscoelastic functions such as the dynamic compliance functions, $B'(\omega)$ and $B''(\omega)$. The comparison was done by computing $B'(\omega)$ from L_m and L_l by

$$\frac{B'(\omega)-B_\infty}{B_\infty}=\int_{-0}^{+\infty}\frac{L_{l,m}(\ln\tau)}{1+\omega^2\tau^2}\mathrm{d}\ln\tau \tag{20}$$

as shown in *Figure 5*. Note that the light scattering $B'(\omega)$ function is lower than the mechanical one, despite the fact that the two have similar shapes and are almost parallel to each other in the dynamic range covered by the light scattering experiment. The lower amplitude in the light scattering $B'(\omega)$ function is due to the smaller relaxation strength α_r, as mentioned above. The longer tail in the mechanical $B'(\omega)$ is introduced by the larger dynamic range obtained via the temperature–time superposition principle. Thus, we believe that we now clearly understand the origin of the difference when comparing the dynamic light scattering with the mechanical relaxation data.

In conclusion, we have shown that the dynamic light spectrum arising from the density fluctuation can be used to determine the compressional compliance with reliability. Using the inverse Laplace transform computer program as developed by Provencher, it is possible to compute a reliable mechanical retardation spectrum from the dynamic light scattering data. We have also shown that for cases where the Williams–Watts function can be used to describe the correlation function, the Contin program also gives an equivalent description.

ACKNOWLEDGEMENTS

C. H. Wang acknowledges partial financial support of the polymer programme of the National Science Foundation and the US Senior Scientist Award provided by the Humboldt foundation. G. Fytas thanks the Max-Planck-Institut für Polymerforschung for a fellowship. E. W. Fischer is supported by the Sonderforschungsbereich 41 of the Deutsche Forschungsgemeinschaft. The authors are indebted to Dr Th. Vilgis for helpful discussions.

REFERENCES

1 Ferry, J. D. 'Viscoelastic Properties of Polymers', 3rd Edn., Wiley, New York, 1980
2 Wang, C. H. and Fischer, E. W. *J. Chem. Phys.* 1985, **82**, 632
3 Wang, C. H., Fytas, G. and Fischer, E. W. *J. Chem. Phys.* 1985, **82**, 4332
4 McKinney, J. E. and Belcher, H. V. *J. Res. Nat. Bur. Stand.* 1963, **67**, 43
5 Drake, P. N., Dill, J. F., Montrose, C. J. and Meister, R. *J. Chem. Phys.* 1977, **67**, 1969
6 Fytas, G., Wang, C. H., Meier, G. and Fischer, E. W. *Macromolecules* 1985, **18**, 1492
7 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Polymer Solids', Wiley, London, 1967
8 Williams, G. and Watts, D. C. *Trans. Faraday Soc.* 1971, **66**, 80
9 Kohlrausch, R. *Pogg. Ann. Phys.* (*4*) 1854, **1**, 56, 179
10 Provencher, S. W. *Comput. Phys. Commun.* 1982, **27**, 213, 229
11 Pollard, H. *Bull. Am. Math. Soc.* 1946, **52**, 908
12 Lindsey, C. P. and Patterson, G. D. *J. Chem. Phys.* 1980, **73**, 3348