Pakistan J. Sci. Ind. Res., Vol. 15, Nos. 4–5, August–October 1972

AN ANALYTICAL METHOD FOR THE DETECTION OF FLUCTUATIONS IN THE TEMPERATURE FUNCTION OF VARIOUS PROPERTIES OF WATER

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(Received October 8, 1971)

Abstract. An analytical procedure has been developed and applied to detect and compare certain 'structure temperatures' in the temperature function of different properties of pure liquid water. These structure temperatures are defined as the temperatures of maxima in the functions of $\triangle I(M,N)\,(T)$, $\triangle f(M,N)\,(T)$, $\triangle(Q^{-1})\,(M,N)\,(T)$, $\triangle\left[\frac{(E^{1}/K)}{1000}\right](M,N)$ (T) and $\triangle(\theta)\,(M,N)\,(T)$.

The form in which the experimental data points are fitted may be written:

$$f(T)=(mT+C)+\sum_{K=1}^{N(<P-2)} C_k \sin K\theta$$

This analytical technique can be applied to uncover the fluctuations in any function.

It has become regular practice to make the assumption that no structure or anomaly is to be found in the temperature variation of various properties of pure liquids and solutions,[1,2] and a smooth curve is chosen to represent a number of discrete experimental points. In some measurements, it is possible to say that the scatter of the data points around a curve are random and the adaption of the smooth curve supplies a reasonably good representation of the actual temperature variation of the property under investigation.

Over the past years, very few properties of liquids and solutions have been measured by any one investigator at temperature intervals of half or one degree centigrade. If one does not expect thermal anomalies, there would be little reason to make more close temperature interval observations.

It is possible to achieve greater precision and accuracy of the observations made at widely spaced temperatures and to seek the best fitting curves to the data points with the help of computer techniques. But a superior approach would be to undertake accurate measurement at closely spaced temperature intervals and the development of a mathematical procedure in order to uncover the structures and to test their repeatability in the temperature functions.

The Analytical Method

The analytical procedure described below may be adapted to detect the fluctuations in the temperature function of a measured property of liquids or the structures in any function. The experimental data points for each run can be Fourier analysed to N terms, where $N=P-2$ and P is the number of experimental data points. The first M (the values of M should be decided by trials) terms are subtracted in order to minimize the low frequency background noise and the series is then synthesized. The procedure amounts to subtraction of a smooth curve from the function leaving a function in which the random errors and any structure are greatly emphasised, so that different runs can be compared with ease. This subtraction of a straight line through the end points of the data before fitting to a Fourier sine series has the effect of improving the convergence of the series (From $1/K$ to $1/K^2$), since both the function and its first derivative are now continuous at the end-points of the range.[3] The analysed function may be symbolized as $(X)\,(M,N)(T)$, where X is the parameter measured.

The form in which the data is fitted may be written.

$$f(T)=(mT+C)+\sum_{K=1}^{N(<P-2)} C_k \sin K\theta$$

where the temperature T is varied in the range $A \leqslant T \leqslant B$, while $\theta = \pi\left(\frac{T-B}{B-A}\right)$ and the constants m, C are so chosen that:

$$f(A)=mA+C \text{ and } f(B)=mB+C$$

For Fourier analysis the temperature range is normalized to (θ, π).

The least-squares fitting for the coefficients C_k can be carried out using a matrix method which does not depend upon equal spacing of the data points.[4]

$$[C_k]_{N\times 1}=[T'T]^{-1}_{N\times N}[T']_{N\times(P-2)}[f_J]_{(P-2)\times 1}$$

where $T_{J,k}=\sin K\theta_J$, $[f_J]$ is the set of measurements $[(f(T)-(mT+C)]$, and the prime after T denotes transposed. The least-squares approximation reduces noise to an extent, determined by N/P, i.e. the ratio of the number of coefficients considered in the Fourier-series to the number of experimental data points.

The choise of N should be governed by the amount of random noise in the measurement. As K increases C_k may be expected to decrease in absolute value until some critical value K_C is reached, after which the average value remains constant; although there is random fluctuation of amplitude and sign. If in

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any case C_k does not decrease to its 'noise' level as K is increased, this must indicate that the temperature intervals are too large, or that the experimental measurements are of insufficient accuracy, or include a level of random error which is too large.

When the coefficients have been determined the data is synthesised with low-frequency back ground removed in the following form:

$$f(M,N)(T) = \sum_{K=M}^{N} C_k \sin K\theta$$

This synthesis effects the removal of the bell-shaped (Fig. 6) curve background to the data and makes possible an accurate positioning of the structure peaks, whether real or arising from random errors; the acid test for the real fluctuations is their repeatability in the measurements. The analysed data-sets are then plotted with P' intervals (where usually $P' > P$ points). This increased number of intervals plotted facilitates the accurate positioning of the structure peaks.

The periodicity analysis may be carried out in order to determine the possible periods of the structure temperatures in the measured properties. This is done by plotting the square of the coefficient C_k against the period $\left[2\,(T_{\text{final}}-T_{\text{initial}})/\text{Coefficient no.}\right]$ in degrees centigrade.

All the computations were carried out on the London University Atlas Computer.

Applications of the Analytical Methods on Experimental Data-Sets and Discussion

The analytical procedure developed in the present communication has been applied to detect 'structure temperatures' of pure liquid water in the measurements of the dielectric properties at 10 cm wavelength band by the absorption (H_{10}—mode) and the E_{010} cavity resonator methods.[5] We shall call the temperatures of maxima of the analysed data-sets the 'apparent structure temperatures' of the properties of liquid water to which they belong. The details of the analysis of the data-sets such as, temperature range of investigation, number of experimental points in a data-set, number of coefficients considered, number of coefficients left out during the analysis and the number of points (intervals) of each run plotted out etc. are given in Tables 1 and 2. In Table 1, $\triangle(Q^{-1})(M,N)(T)$, $\triangle f(M,N)(T)$ and $\triangle I(M,N)(T)$ are approximately the functions of ε'', ε_s or ε' and ε'' respectively; where ε' and ε'' are the real and imaginary parts of the complex permittivity $\bar{\varepsilon}$ and ε_s is the static dielectric constant. Therefore, the fluctuations or the structure temperatures (Figs. 3, 2 and 1) in the temperature function of $\triangle f(M,N)(T)$ are those present in ε' and the anomalies appearing in $\triangle(Q^{-1})(M,N)(T)$ and $\triangle I(M,N)(T)$ are related to ε''.

Table 2 shows the application of the analytical method to the data-sets collected by Ahsanullah and Qurashi [6–8] in their investigations of the intermolecular potential energy of activation for the viscous flow[6] $\triangle[(E^1/K)/1000)](M,N)(T)$, the refractive index[7]

TABLE 1*

No. of experimental data-set	Figs. no	Temperature range of investigation (°C)	The plot of (X) (M, N) (T)	No. of experimental points (P)	No. of coefficients considered (N)	No. of coefficients left out during the analysis (M)	No. of points plotted (P′)	Remarks
1	1	25–70	$\triangle I(M,N)(T)$	87	74	5	134	No smoothing ($NP \lessapprox 2$)
2	2	12–70	$\triangle(Q^{-1})(M,N)(T)$	117	115	5	175	,,
3	3	,,	$\triangle f(M,N)(T)$	,,	,,	5	,,	,,
4	4a	25–70	Periodicity: (Coeff.)^2 against $[2(T_f-T_i)/\text{Coeff. No.}]$	87	40	5	—	—
5	4b	12–70	,,	117	40	5	—	—

*Ref. 5

TABLE 2*

No. of experimental data-set	Figs. no	Temperature range of investigation (°C)	The plot of (X) (M, N) (T)	No. of experimental points (P)	No. of coefficients considered (N)	No. of coefficients left out during the analysis (M)	No. of points plotted (P′)	Remarks
1	5	32·2–74·2	$\triangle\left\{\frac{(E^1/K)}{1000}\right\}(M,N)(T)$	41	20	2	99	Smoothing $N \approx (P-2)/2$
2	6	11–50	$\triangle(\theta)(M,N)(T)$	40	25	0	99	,,
3	7	6·22–72·6	$\triangle\left\{\frac{(E^1/K)}{1000}\right\}(M,N)(T)$	48	25	2	149	,,

*Ref. 6–8

$\triangle^{(\theta)}$ $(M,N)(T)$ and mutual potential energy of molecules[8] $\triangle[(E^{\mathrm{I}}/K)/1000]$ $(M,N)(T)$ of pure liquid water which are shown in Fig. 5, 6 and 7 respectively. Here again the analysed data-sets revealed the fluctuations in the temperature functions of the above parameters.

The structures detected in $\triangle(Q^{-\mathrm{I}})$ (T), $\triangle f(T)$ and $\triangle I(T)$ are approximately represent 3–6% of their respective values; whereas in the plots of untreated data-sets[5] the scatter of the data-points in a run was in between 0.5–1%. It was found that the average value of the drop between steps was 0.08 units of $(E^{\mathrm{I}}K)/1000$ in its temperature function;[8] whilst the analysed data-set in Fig. 7 shows drops from maxima to minima from 1 to 4 units of the arbitrary value of the function $[(E^{\mathrm{I}}/K)/1000)]$ $(M,N)(T)$.

Another advantage of the analytical method developed is that during division or multiplication of data-points of the sets of different measured para-

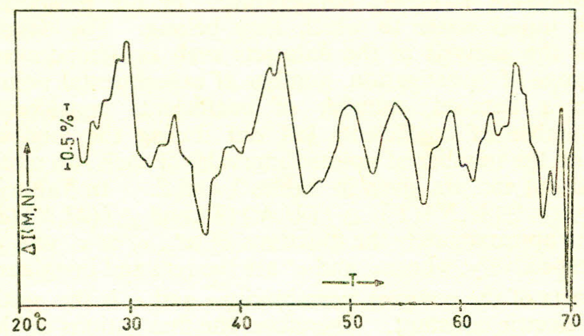


Fig. 1. Plot of $\triangle I$ (M,N) (T), average of six runs.

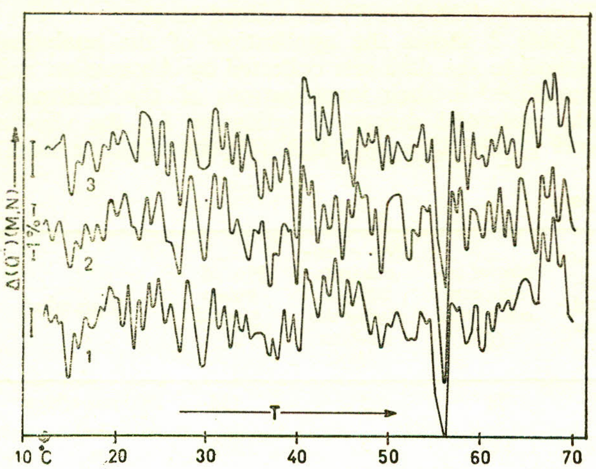


Fig. 2. Plot of Δ $(Q^{-\mathrm{I}})$ (M,N) (T) of three runs.

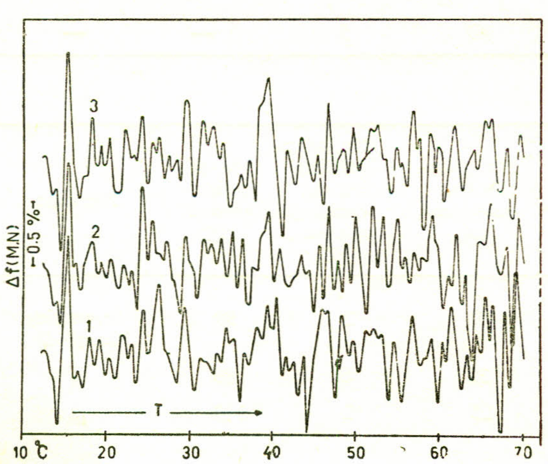


Fig. 3. Plot of Δf (M,N) (T) of three runs.

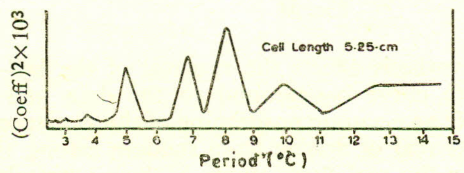
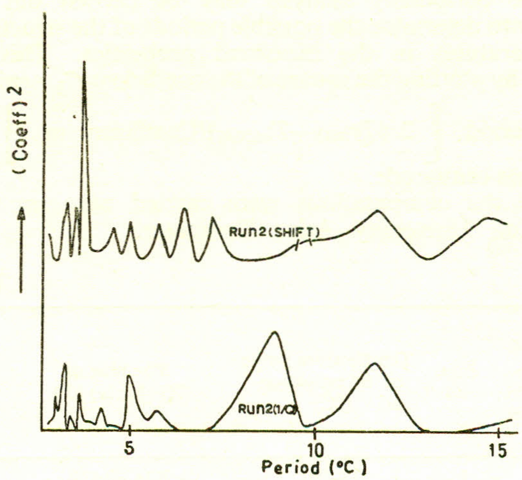


Fig. 4a. The periodicity of sturcture temperatures in $\triangle I$, period in degrees centigraade.



4b. The periodicity of structure temperatures in Δf and $\Delta(Q^{-\mathrm{I}})$, period in degrees centigrade.

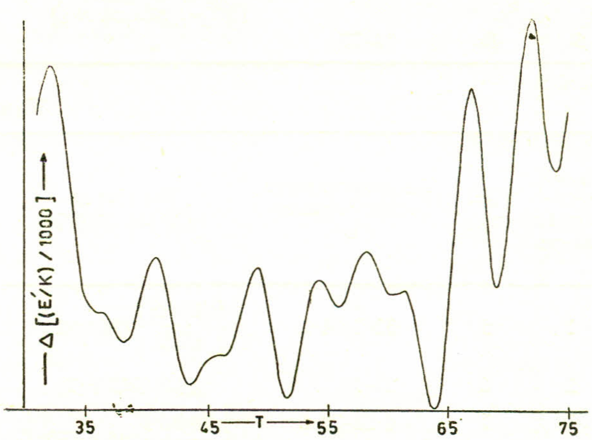


Fig. 5. Plot of $\Delta\left[\frac{(E^{\mathrm{I}}/K)}{1000}\right]$ (M,N) (T).

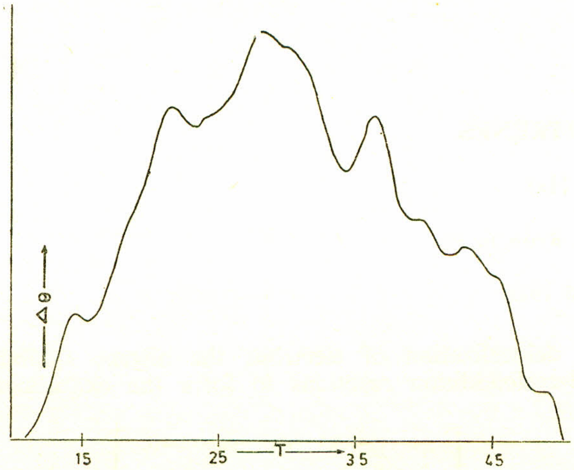


Fig. 6. Plot of Δ (θ) (M,N) (T).

meters[5] or averaging the runs of same parameter (Fig. 1) only an accurate reading of temperature is required, and the intervals between readings need not be exactly equal.

Acknowledgements. I wish to express my special thanks to my supervisor Professor J.B. Hasted whose interest and invaluable experience have contributed such a great deal to the success of the project. The help of Mr. L. Moore, in the analytical technique, is gratefully acknowledged. Thanks are also due to London University Atlas Computer. I am grateful to P.C.S.I.R. for granting the study leave.

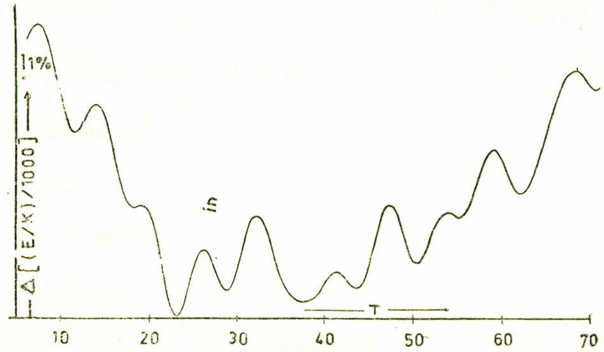


Fig. 7.Plot of $\Delta\left[\frac{(E^{I}/K)}{1000}\right]$ (M,N) (T).

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