A MACROSCOPIC APPROACH TO FLUCTUATION ANALYSIS

SOLUTION OF THE PHASE PROBLEM OF RELAXATION SPECTROMETRY

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One of us (1) has demonstrated that by multivariate spectral analysis of the statistical mechanical noise and fluctuations about equilibrium, one may obtain all relevant rate parameters (including Onsager coefficients) from the power spectral matrix and its inverse at $f = 0$. The proof is based on the fluctuation-dissipation theorem of Callen and co-workers (2, 3) and in canonical systems (systems of chemical interest), the fundamental equation is

$$\Omega \equiv L\Phi = 4 < \delta\vec{\alpha}\, \delta\vec{\alpha}^* > \{G(0)\}^{-1} = 4 \int_0^\infty G(f)\, \mathrm{d}f \{G(0)\}^{-1}, \tag{1}$$

where Ω is the reduced matrix of rate coefficients, defined in terms of an exactly determined set of progress variables (4), L is the Onsager flow matrix, Φ is the matrix of second partials of free energy with respect to the extensive thermochemical parameters, $G(f)$ is the spectral matrix, and $< \delta\vec{\alpha}\, \delta\vec{\alpha}^* >$ is the matrix of second moments of the extensive parameters.

The above equation is also macroscopically applicable to a relaxation process of Langevin form

$$\frac{\mathrm{d}\delta\vec{\alpha}}{\mathrm{d}t} + L\Phi\delta\vec{\alpha} = \vec{\chi}(t); \quad < \vec{\chi}(t) > = 0 \tag{2}$$

where $\vec{\chi}(t)$ is a random force induced by a Gaussian white noise pertubation of some intensive thermochemical parameter (T, P, E, M, etc.). It can be proven that solution of the spectral equation then reduces to Eq. 1, if the pertubations are sufficiently small as to allow the approximation of linearity.

Experimentally, this allows one to solve, using simple algebraic matrix methods, all rate parameters within a system. Since time series averaging in the frequency domain is employed, one can use Wiener and subsequent stochastic analysis theory (5, 6) to draw kinetic noise from extraneous noise through the use of spectral averaging. In fact, there is (in principle) no limitation (to the Heisenberg limit) to the kinetic information that can be extracted. Thus, it might be possible even to measure the intrinsic statistical mechanical fluctuations in a variety of systems. Some possible approaches are discussed.

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AN INEXPENSIVE MICROCOMPUTER-BASED STOPPED-FLOW DATA ACQUISITION SYSTEM

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ABSTRACT A low-cost (<$2,500) microcomputer-controlled data acquisition system for use with a stopped-flow instrument is described. Data acquisition, reduction, signal averaging, kinetic modeling, and plotting are performed under software control. Applications to biological and inorganic systems are presented.

INTRODUCTION

Kinetics studies typically generate enormous amounts of raw data that traditionally have been laboriously hand-digitized and reduced. The described microcomputer-controlled data acquisition system improves accuracy, eliminates the labor-intensive steps, and permits data acquisition, reduction, and plotting of final results in seconds without the operator ever having to handle raw data.

METHODS

Instrumentation

The stopped flow instrument has been described previously (1). In all experiments reported concentrations are before mixing.

The computer system consists of an MITS Altair 8800 microcomputer (Altair Corp., Chicago, Ill.) using an Intel 8080A microprocessor (Intel Corp., Santa Clara, Calif.), 9,216 bytes of semiconductor random access memory, 2,048 bytes of permanent read-only memory (PROM), and an ASR33 Teletype interface (Processor Technology 3P+S serial card). The data acquisition control and clock circuitry plugs directly into the Altair bus; it uses ~50 7400 type small and medium-scale integration integrated circuits and was wire-wrap constructed on a Vector 8800V prototyping card (Vector General, Inc., Woodland Hills, Calif.). The separate analog card contains a Hybrid Systems ADC-550-10E-G 10 bit, 27-μs analog-to-digital converter (ADC) (Hybrid Systems Corp., Burlington, Mass.) and two 3711-10 10-bit digital-to-analog convertors (DAC's), which communicate with the control card through multiconductor cables. The real-time clock controls the conversion rate of the ADC and is selectable in a 1, 2, 4, 5, 8, 10, 16 sequence from 40 μs to 160 s per data point.