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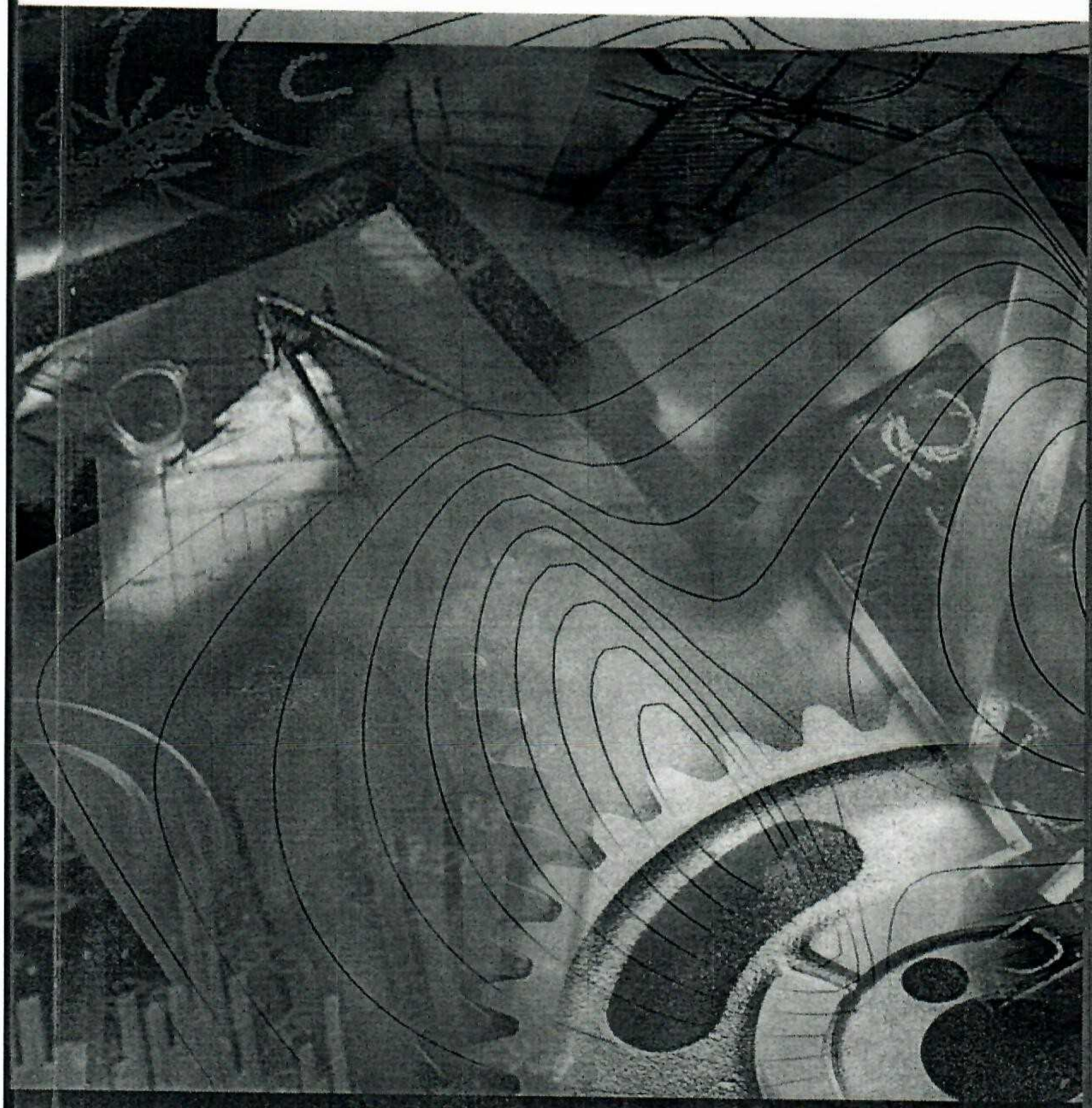

R.L. May, G.F. Fitz-Gerald and I.H. Grundy

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Analysis of the Performance of Two Distance Geometry Algorithms in Simulation of Polymer Systems

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1 Introduction

The development and testing of efficient algorithms for microscopic, atomistically detailed models of polymers and composites is an important direction in many new industrial materials technologies. Amongst most popular methodologies for the construction of such algorithms are the Molecular Dynamic (MD) and Monte-Carlo (MC) simulations. Both of these methodologies have well-known weaknesses. Since polymers are characterised by a wide-range hierarchy of different length and time scales, in MD simulations of a long-chain polymer the system often remains trapped within the neighbourhood of the initial configuration which leads to insufficient samplings of the configuration space and unreliable estimations of the dynamic and structural properties of the polymer. In some cases, recently proposed MC algorithms can achieve a higher efficiency of configurational sampling, but these algorithms represent a real alternative to the MD methodology only in the case when static (rather than dynamic) properties of the material are of the main interest. For all currently available methodologies the problem of finding an adequate initial sampling is of critical importance. This problem is the main focus of this paper.

2 Distance Geometry Problem: Why Do We Need New Approaches?

We aim at recovering positions $x^1, ..., x^N \in \mathbb{R}^3$ of atoms of polymer structures from the given lower, l_{ij}, and upper, u_{ij}, bounds on the distance constraints, i.e.

$$l_{ij} \leq \|x^i - x^j\| \leq u_{ij}, \quad (i,j) \in \mathcal{S},$$

where $\mathcal{S}$ is a subset of all atom pairs (say, $i, j = 1, ..., n$, $n \leq N$). Such a recovery assumes a generation of a *representative sample* of local minimisers of the chosen objective function F and can be performed via the solution of the optimisation problem

$$F(\mathbf{x}) \to \min, \quad \mathbf{x} \in \mathbb{R}^{3N}. \qquad (1)$$

This problem, referred to as the distance geometry (DG) problem, is not new and a number of methods for its solution already exist, e.g. metric matrix methods, embedding algorithms, torsional space methods etc. These methods have provided important tools in molecular modelling applications ranging from conformations of small molecules, protein and peptides to the time-averaged conformations of biological macromolecules, pharmacophore modelling and drug-receptor docking [2, 8, 6]. In most of these applications the conformational space is searched by generating a large number of independent solutions within the constraints of the model, and each structure is then evaluated for the inclusion in the final ensemble of low-energy conformations, using a force field or other energetic evaluations. Using such classical algorithms, the answer to the question on the existence of a model that satisfies our experimental constraints comes at a cost of dealing with (a) $\sim \frac{1}{2}(N-1)N$ nonbonded terms (for structures of N atoms) [4], (b) $\sim 2N^2$ units of memory,(c) computationally costly smoothing techniques [6].

In order to be successful in modelling complex polymer and composite systems the computational efficiency of distance geometry procedures used at the initial stage of molecular modelling should be improved. Since it becomes clear (see, for example, [8] and references therein) that such procedures have potential in the computer-aided molecular design where polymers and composites worthy of actual synthesis can be effectively predicted, in the last few years there has been an increasing interest to the development of such improved procedures. In the process of computer-aided molecular design the distance geometry and the molecular dynamics procedures can be considered as complementary methods [2] in a sense that efficient DG procedures can generate complex models rapidly at relatively small computational cost and produce structures that become an appropriate starting point for molecular mechanics and dynamics calculations [9]. Although results on MD computations applied to polymers and composites are extensive, applications and analysis of improved DG procedures are still lacking in the literature.

3 Choices of the Objective Function and Algorithms Based on Its Smoothing

Typical choices of the objective function aim at making each term responsible for a specific constraint either zero, if the constraint is satisfied, or monotonically (increasingly) positive, as the violation of the constraint increases. This can be achieved for functions taken in the form

$$F(\mathbf{x}) = \sum_{(i,j)\in\mathcal{S}} \epsilon_{ij}, \text{ or } F(\mathbf{x}) = \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} \epsilon_{ij}, \qquad (2)$$

where $\epsilon_{ij} : \mathbb{R}^n \to \mathbb{R}$. A particular example includes $\epsilon_{ij} = \max^2[0, (d_{ij}^2 - u_{ij}^2)] + \max^2[0, (l_{ij}^2 - d_{ij}^2)]$ with $d_{ij} = \|\mathbf{x}^i - \mathbf{x}^j\|_2$, and many other examples (including non-differentiable functions) can be found in the literature (see [2], e.g.). In this section we use the following function

$$\epsilon_{ij} = \min^2\left[0, \left(\frac{d_{ij}^2}{l_{ij}^2} - 1\right)\right] + \max^2\left[0, \left(\frac{d_{ij}^2}{u_{ij}^2} - 1\right)\right]. \qquad (3)$$

All typical choices of ϵ_{ij} lead to too many minimisers for any realistic structures. It is natural, therefore, to try to transform the original objective function to a smoother function that have a smaller number of local minimisers, and then to trace back those minimisers to the original objective function. In the Wu-Moré method [7] the objective function is also taken in the standard form (2), (3). In this case the coordinates $\mathbf{x}^1, ..., \mathbf{x}^N$ from the representative sample should satisfy the following inequalities

$$\left|\|\mathbf{x}^i - \mathbf{x}^j\| - \delta_{ij}\right| \le \epsilon, \quad (i,j) \in \mathcal{S}. \qquad (4)$$

For fixed $\epsilon > 0$ and $\delta_{ij} \in [l_{ij}, u_{ij}]$ this leads to the problem of finding ϵ-optimal solutions to our distance geometry problem which is known to be a NP-hard problem [7].

With the Gaussian transform $g \in \mathbb{R}^n \to \mathcal{G}^\lambda(g) \in \mathbb{R}$

$$\mathcal{G}^\lambda(g) = \frac{1}{\pi^{n/2}\lambda^n}\int_{\mathbb{R}^n} g(\mathbf{y}) \exp\left(-\frac{\|\mathbf{y}-\mathbf{x}\|^2}{\lambda^2}\right) d\mathbf{y} \quad (5)$$

we transformed our objective function F defined by (2), (3) to a smoother function (with controlled degree of smoothing) with fewer local minimisers, then apply an optimisation algorithm to the transformed function, and finally trace the minimisers back to the original function [7]. For functions representable in the form $F(\mathbf{x}) = \sum_{(i,j)\in\mathcal{S}} h_{ij}(d_{ij})$ (in our case $h_{ij}(d_{ij}) \equiv \epsilon_{ij}$ given by (3)) the specific analytical representation of $\mathcal{G}^\lambda(F)$ is known [7] and can be approximated with the Gauss-Hermite approximation (say, with q nodes) with function $\mathcal{G}^{\lambda,q}(F)$. Then, in order to determine local minimisers of the transformed function for different values of λ, $\bar{F} = \mathcal{G}^{\lambda_k,q}(F)$, $k = 0, 1, ..., p$ ($\lambda_0 > \lambda_1 > ... > \lambda_p$ and the original function is recovered in the limit $\lambda_p \to 0^+$), we follow [7] in using the quasi-Newton-type algorithm

$$\mathbf{x}_{k+1} = \mathbf{x}_k - \alpha_k H_k \nabla\bar{F}(\mathbf{x}_k), \quad k = 0, 1, ..., p \quad (6)$$

with a given approximation H_k of the inverse Hessian (k is the number of the current iteration), a randomly chosen $\mathbf{x}_0$, and $\alpha_k > 0$. The quality of the result is judged upon the error function $\epsilon_l^u = \max(\epsilon_l, \epsilon_u)$ where

$$\epsilon_l = \min\left(\frac{d_{ij}}{l_{ij}-1}, 0\right), \quad \epsilon_u = \max\left(\frac{d_{ij}}{u_{ij}-1}, 0\right),$$

and the corresponding value of the objective function.

A typical result of computation with this algorithm, obtained for a short-chain polyethylene structure consisting of 250 backbone carbon atoms (polymer $-CH_2 - CH_2-$ with 3-atom structural unit $-CH_2-$), can be found in [6]. Such structures correspond to alkane liquids and important for petrochemicals and lubricants.

In experimenting with this distance geometry algorithm no bound-smoothing procedures have been implemented. Such smoothing procedures, used in classical distance geometry algorithms, are usually implemented to lower some (unrealistic) default upper bounds in the constraints with the triangle inequality and to raise some (unrealistic) default lower bounds with the inverse triangle inequality. Although this step aims at achieving a better sampling of the conformational space, it leads to a high computational cost due to the increased number of effective constraints and the decrease in the regularity properties of the potential function. Despite the elimination of the bound-smoothing step, our experiments with larger chains and increased number of atoms showed that the algorithm described in this section is still computationally expensive. Although very reliable in calculating individual chains isolated in space, the algorithm needs further improvements in application to more complex structures.

Since in materials context the bulk properties are the basis of the economic value of the material, we have to be able to deal with bulk materials simulated by a large collection of molecules. In the next section we describe an efficient distance geometry algorithm capable of dealing with such materials.

4 Periodic boundary conditions and modelling bulk materials

The methodology described in the previous section is well suited for the analysis of the behaviour of a single chain isolated in space. However, in the case of bulk polymers and composites where the effect of entangled networks is markedly pronounced, the efficiency of this methodology decreases.

In order to overcome this difficulty we apply the experimental density simulation-box technique where, as the name suggests, we packed chains into a simulation box at the experimental density. Instead of picking up distances randomly (between lower and upper bounds), as we have done in the previous section, we pick up 3D coordinates within a chosen periodic cell creating by periodic boundary conditions. In this case we do not compress the structure, as in the classical embedding algorithms, due to its projection from $N-1$ dimensions to three dimensions. To achieve a higher homogeneity of the resulting structure, we prescribe minimum and maximum bounds on the distance between *each* pair of atoms. These bounds are used then to define bond lengths and bond angles between neighbouring atoms, and the minimum separation of non-bonded atoms. In constructing the code, it has been assumed that atoms in different molecules can be treated as hard spheres and they have a minimum separation corresponding to a non-overlap condition which leads to the obvious condition for default lower bounds. The default maximum separation can be essentially arbitrary, but in some cases the assumption that all random points are confined to an "amorphous" cube can lead to "natural" default upper bounds (typically taken as the half of a diagonal of the cubic cell). Atoms in the same molecules separated by many bonds (≥ 3) are treated in our code in the same way as atoms in different molecules (i.e. non-bonded) which leads naturally to the situation where in some case nonbonded neighbours are closer than bonded neighbours. By creating a representative cell of the system and replicating it periodically in all direction in space [4], we begin simulations with random atom coordinates within this "central" cell with periodic boundary conditions. The size of the cell, taken as cubic, is determined by the density of material.

The basic idea of our algorithm is similar to classical procedures [3, 2] and consists of minimising the error function by generating random conformers and then refining the obtained coordinates against an error (objective) function chosen in this section in the form of (2) with

$$\epsilon_{ij} = \max(l_{ij} - d_{ij}, d_{ij} - u_{ij}). \qquad (7)$$

The main difference of the proposed algorithm compared to classical DG procedures is in a number of steps taken to achieve savings in computational time for producing better starting conformations, in the sense that subsequent minimisation of the error function more often succeeds in reaching a value close to zero. Compared to classical distance geometry algorithms such as the metric matrix DG our algorithm is considerably simpler. In fact, we do not base our constructions on computing (three) largest positive eigenvalues and corresponding eigenvectors of the trial matrices which correspond to some conformations in $\mathbb{R}^n$ and converting such matrices into a set of trial coordinates in $\mathbb{R}^3$.

The main steps of our algorithm are as follows

- We select an atom from the given list at random (let it be, say, atom i);
- We calculate the distance between this atom and *each* other atoms;
- If the calculated distance falls outside of the prescribed bounds, we calculate the differences (the bound errors) according to (7), and identify the largest of such bound errors (attained, say, for atom j);
- Then we move atom i along the path $i - j$ in order to satisfy the prescribed bounds by sampling the new distance randomly from a quadratic distribution between the minimum and maximum bounds (i.e. using a uniform distribution in $\mathbb{R}^3$);
- We repeat the above procedure for all atoms until all bounds are satisfied.

This algorithm has been tested for a number of bcc and fcc lattices and allowed to obtain quickly initial topologies for structures many times larger than those reported in the previous section. Most experiments have been performed with long (over 1000 backbone atoms) linear alkanes, confined to a periodic cell, i.e. bulk polyethylene (solid or liquid).

Since for many realistic polymer and composite systems we have to deal with many chains confined to one molecular structure, a number of results have been obtained for bulk linear polyethylene (for example, structures constructed from 10 chains of 150 backbone carbon atoms each).

As an example, in Fig. 1 we demonstrate the results of computation for bulk decane (decane molecule is ethylene's derivative with the degree of polymerisation equal 5) $C_{10}H_{22}$ simulating with 30 molecules confined to a periodic cell 21.3331 Å at density $\rho = 0.73 \mathrm{g/cm}^3$ and temperature 300°K.

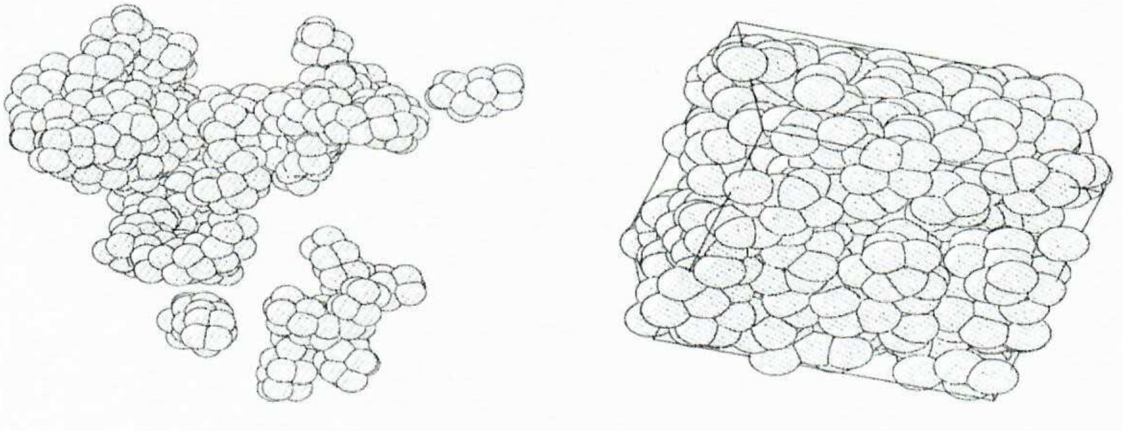

FIGURE 1. A member of the representative sample for bulk decane simulated by 30 molecules (periodic boundary conditions, all constraints); unpacked (left) and packed (right)

Although hydrogen atoms are often omitted from consideration by assuming that their positions can be well approximated and they can be added latter by "decorating" the structure (this idea was used in the previous groups of experiments), our code takes hydrogen atoms into account via packing constraints for this particular case. Since decane can produce a wide spectrum of volatile hydrocarbon products on degradation [1], we plan to investigate the effect of inclusion of hydrogen atoms into the model further. As it can be seen from Fig. 1 generated structures are sufficiently homogeneous to be relaxed efficiently with molecular dynamics codes, and we shall present the results of the MD refinement of these structures elsewhere.

The obtained conformations were analysed using the concepts of pair correlation (i.e. radial distribution functions), dihedral distribution, radius of gyration, cohesive energy, free volume, and Voronoi statistics. In particular, the radial distribution function for the conformation shown in Fig. 1 confirmed the presence of 2 peaks, one at 1.54 A, and the other at 2.52 A, as expected.

In modelling complex polymer and composite systems it is important to achieve a high level of vectorisation of computational procedures. Using NEC SX-4, we monitored the level of vectorisation of the algorithm presented in this section in a series of model experiments reported here. In particular, generating a representative sample of 10 structures for a 1500-atom model (10 chains, 150 backbone carbon atoms each) took 1302 sec with the level of vectorisation exceeding 99%. A similar computation for the decane model required 4876 sec with vectorisation 99.5%.

5 Conclusions and future directions

We considered efficient distance geometry algorithms capable of dealing effectively with individual polymer chains isolated in space, as well as with large material structures, including bulk materials. By providing good approximations to topological molecular structures of materials such algorithms can increase the efficiency of available molecular modelling codes and therefore can lead to the possibility of calculating structural and mechanical properties of polymer and composite structures using available methodologies [5]. As a development of the presented work we are now undertaking a comparison of the performance of several distance geometry algorithms for simulating bulk molecular cross-linked structures using end-to-end distributions, radii of gyration, and radial distribution functions.

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Contents

Invited Papers

The Interaction of Aerodynamics, Structural Dynamics and Control in the Design of Modern Aircraft
Moti Karpel . . . 3

Stabilities, Transitions, Trends and Noise in Mathematics and Statistics in Engineering Education
Helen MacGillivray . . . 13

Responding to SARTOR 3
Leslie Mustoe . . . 21

Preconditioning Legendre Spectral Collocation Methods for Elliptic Problems
Seymour V. Parter . . . 27

Making Mathematics Relevant: Why isn't Filtration Theory an Engineering Reality?
Peter J. Scales, Ross G. De Kretser, Kerry A. Landman, Daniel Lester and Shane P. Usher . . . 33

Contributed Papers

Calculation of Phase Separation for Polymers in Solution
J.M. Aitchison and R.E.J. Norgate . . . 43

Exploring Mathematical Concepts with MATLAB and Java Graphical User Interfaces
Geoffrey K. Aldis . . . 47

Sensitivity Problems for Multiple Eigenvalues in Structural Analysis
Alan L. Andrew . . . 51

Estimation of Ore:Coke Distribution Across the Burden Surface in a Blast Furnace
P.R. Austin, S.J. Chew and P. Zulli . . . 55

On the Free Vibration of Elastic–Plastic Shallow Shells
M.M. Banerjee, S. Chandra, Jagannath Mazumdar and Brandon Pincombe . . . 59

Non-Linear Modelling of Space Tethers and Application to Deployment, Retrieval and Electrodynamic Operations
Chris Blanksby . . . 63

Finite Element Prediction of Radar Cross Sections
Austin Mack . . . 195

The Dynamics of Reaction Diffusion Equations Lead to a Holistic Discretisation
T. MacKenzie and A.J. Roberts . . . 199

Application of a Model Reduction Method to a Forced Non-Linear Dynamic System
A. Manfredini and P. Vigni . . . 203

Synthesis of Planar Linkages using Natural Coordinates and a Genetic Algorithm
A. Manfredini and P. Vigni . . . 207

Spectral Analysis of Heart Sounds and Vibration Analysis of Heart Valves
J. Mazumdar . . . 211

Investigations of the Vibrational Behaviour of Cylindrical Forms with Application to Musical Instrument Design
N.M. McLachlan and B. Keramati Nigjeh . . . 215

Accounting for Thermal Effects in Dynamics of Piezoelectric Structures
Roderick V.N. Melnik . . . 219

Analysis of the Performance of Two Distance Geometry Algorithms in Simulation of Polymer Systems
Roderick V.N. Melnik, Alfred Uhlherr and Frank de Hoog . . . 223

Wind Tunnel Study of a Symmetrical Wing with Tip Sails
Mushtak Talib Ali Al-Atabi and Talal F. Yusaf . . . 227

Modelling the Shear Deformation of Fabric for Composite Automated Manufacture
Minh Nguyen and Israel Herszberg . . . 231

Designing and Managing Networks for Self-Similarity
Sven Östring, Harsha Sirisena and Irene Hudson . . . 235

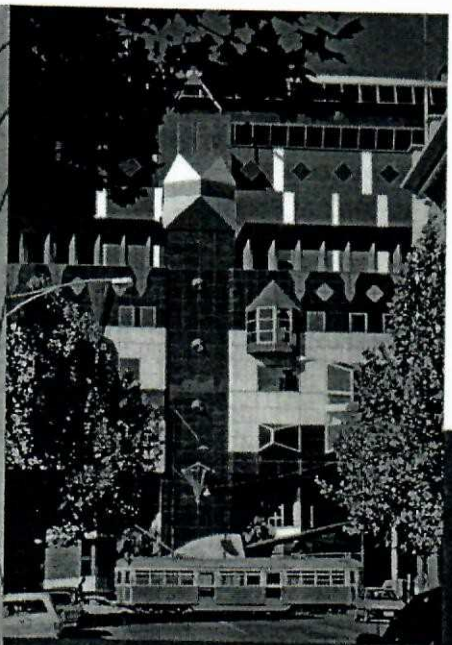
The Pressure Field in a Two-Dimensional Taper-Taper Gas-Lubricated Bearing of Narrow Geometry
Irene Penesis, John Shepherd and Howard Connell . . . 239

Flight Data Filtering using Truncated Singular Value Decomposition
Adam Randall, Tao-Minh Lee and Robert Hood . . . 243

Deflection of a Pretensioned Circular Diaphragm due to Aerothermal Loading
S. Ahmad Sharifian and David R. Buttsworth . . . 247

A Simple Combustion Process in a Semibatch Reactor
Harvinder S. Sidhu, Mary J. Sexton, Mark I. Nelson, Geoffry N. Mercer and Rodney O. Weber . . . 251

A First Year Calculus Course for Engineering Students
Geoff Smith and Leigh N. Wood . . . 255



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