NOTICE: Ensuring subscriber access to content on IOPscience throughout the coronavirus outbreak - see our remote access guidelines.

Table of contents

Volume 30

Number 35, 5 September 2018

◂ Previous issue Next issue ▸

Buy this issue in print

View all abstracts

Topical Review

Special Issue Papers

Papers

Surfaces and interfaces

Nanostructures and nanoelectronics

Structure, dynamics and phase transitions

Electronic structure

Correlated electron systems

Physics of materials

Magnetism

Computational and experimental methods

Temperature dependence of the Young’s modulus of polymers calculated using a hybrid molecular mechanics–molecular dynamics method 355901

Iwan H Sahputra, Alessio Alexiadis and Michael J Adams

+ View abstract View article PDF

JOURNAL LINKS

Submit an article

About the journal

Editorial Board

Author guidelines

Review for this journal

Publication charges

News and editorial

Awards

Journal collections

Pricing and ordering

Contact us

Editorial board

Journal of Physics: Condensed Matter is led by an Executive Board comprising of the Editor-in-Chief and ten Section Editors, who oversee the wider Editorial Board.

Editorial board
Surfaces and Interfaces
Soft Matter, Biophysics, and Liquids
Physics of Chemical Processes
Nanostructures and Nanoelectronics
Structure, Dynamics, and Phase Transitions
Electronic Structure
Correlated Electron Systems
Physics of Materials

Editor-in-Chief

Gianfranco Pacchioni Universitá degli Studi di Milano-Bicocca, Italy

---

Surfaces and Interfaces

Section Editor

Steven Schofield University College London, UK

Editorial Board

Matthias Batzill University of South Florida, USA

Shixuan Du Chinese Academy of Sciences, China

Christoph Tegenkamp TU Chemnitz, Germany

Soft Matter, Biophysics, and Liquids

Section Editor

Gerhard Kahl TU Wien, Austria

Editorial Board

Ana Laura Benavides University of Guanajuanto, Mexico

Pietro Cicuta University of Cambridge, UK

Matthias Fuchs Universitat Konstanz, Germany

Beatrice Ruta Lyon 1 University, France

Joel Stavans Weizmann Institute of Sciences, Israel

Paulo Teixeira ISEL and Universidade de Lisboa, Portugal

Limei Xu Peking University, China

Physics of Chemical Processes

Section Editor

Talat S Rahman University of Central Florida, Orlando, USA

Editorial Board

Jonas Björk Linköpings University, Sweden
Pavel Jelinek Czech Academy of Science, Czech Republic
Alexei A Kornyshev Imperial College London, UK
Xinzheng Li Peking University, China
Jianmin Ma Hunan University, China
Natalia Martsinovich University of Sheffield, UK

Nanostructures and Nanoelectronics

Section Editor

Thomas Frederiksen Donostia International Physics Center, Spain

Editorial Board

Denis Basko CNRS, France
Jon P Bird University at Buffalo, The State University of New York, USA
Shixuan Du Chinese Academy of Sciences, China
Pavel Jelinek Czech Academy of Science, Czech Republic
Mikhail Katsnelson Radboud University Nijmegen, The Netherlands
Zhi-Min Liao Peking University, China
Hai-Zhou Lu Southern University of Sciences and Technology, China
Jing-Tao Lu Huazhong University of Science and Technology, China
Juliana Morbec Keele University, UK
Paola de Padova CNR, Italy

Structure, Dynamics, and Phase Transitions

Section Editor

Peter A Dowben University of Nebraska at Lincoln, USA

Editorial Board

Bing-Yang Cao Tsinghua University, China
Richard Dronskowski RWTH Aachen University, Germany
Chun-Gang Duan East China Normal University, China
Robert Jones University of Nottingham, UK
Oana Cojocaru-Mirédin Aachen University, Germany
Xiaoshan Xu University of Nebraska at Lincoln, USA
Yansun Yao University of Saskatchewan, Canada

Electronic Structure

Section Editor

Jin Zhao University of Science & Technology of China, China

Editorial Board

Alexey Akimov University at Buffalo, USA
Lilia Boeri Graz University of Technology, Austria
David Bowler University College London, UK
Michele Pavanello Rutgers University, USA
Paola de Padova CNR, Italy
Andre Schleife University of Illinois at Urbana-Champaign, USA

Correlated Electron Systems

Section Editor

Krishnendu Sengupta Indian Association for the Cultivation of Science, India

Editorial Board

Ryotaro Arita RIKEN, Japan
Annica Black-Schaffer Uppsala University, Sweden
David Logan University of Oxford, UK
Jiannis Pachos University of Leeds, UK
Babak Seradjeh Indiana University, USA
Pratap Raychaudhuri Tata Institute of Fundamental Research, India

---

Physics of Materials

Section Editor

Jinguang Cheng, Institute of Physics, Chinese Academy of Sciences, China

Editorial Board

Jaakko Akola Norwegian University of Science and Technology, Trondheim, Norway
Hong-Gang Luo Lanzhou University, China
Kee Hoon Kim Seoul National University, Korea

Magnetism

Section Editor

Je-Geun Park Seoul National University, South Korea

Editorial Board

Saswati Barman Institute of Engineering and Management, Kolkata, India
Kee Hoon Kim Seoul National University, Korea
Young-June Kim University of Toronto, Canada
Peter Holdsworth Ecole Normale Supérieur de Lyon, France
Anriban Misra North Bengal University, India
Kirrily Rule Australian Nuclear Science and Technology Organisation, Australia
Christopher Stock Edinburgh University, UK
Ross Stewart ISIS Neutron and Muon Source, UK

Computational and Experimental Methods

Section Editor

Maria-Carmen Asensio Synchrotron SOLEIL, France

Editorial Board

Denis Basko CNRS, France
David Bowler University College London, UK
Carlo Mariani Universita di Roma 'La Sapienza', Italy
Maosheng Miao Beijing Computational Science Research Center, China
David Strubbe University of California Merced, USA

Peer-Review Advisory Panel

Journal of Physics: Condensed Matter also has a **Peer Review Advisory Panel**.

Back to top

Journal of Physics Condensed Matter

COUNTRY

United Kingdom

Universities and research institutions in United Kingdom

SUBJECT AREA AND CATEGORY

Materials Science
└ Materials Science (miscellaneous)

Physics and Astronomy
└ Condensed Matter Physics

PUBLISHER

IOP Publishing Ltd.

H-INDEX

233

PUBLICATION TYPE

Journals

ISSN

09538984, 1361648X

COVERAGE

1989-2021

INFORMATION

Homepage

How to publish in this journal

jpcm@ioppublishing.org

SCOPE

Journal of Physics: Condensed Matter covers the whole of condensed matter physics including soft matter, physics of chemical processes, and method development. Papers may report experimental, theoretical or computational studies.

Join the conversation about this journal

FIND SIMILAR JOURNALS

1	2	3
Physical Review Materials	European Physical Journal B	Progress in Surface Science
USA	DEU	GBR
97% similarity	92% similarity	89% similarity

← Show this widget in your own website

Just copy the code below and paste within your html code:

`<a href="https://www.`

SCImago Graphica

Explore, visually communicate and make sense of data with our new data visualization tool.

Metrics based on Scopus® data as of April 2022

Alexander 3 years ago

Homepage link does not work.

reply

Melanie Ortiz 3 years ago SCImago Team

Dear Alexander,

Thank you for reporting that error. We have updated the journal's website information (see just above). Best Regards, SCImago Team

Leave a comment

Name

Email
(will not be published)

Submit

The users of Scimago Journal & Country Rank have the possibility to dialogue through comments linked to a specific journal. The purpose is to have a forum in which general doubts about the processes of publication in the journal, experiences and other issues derived from the publication of papers are resolved. For topics on particular articles, maintain the dialogue through the usual channels with your editor.

Developed by: Powered by:

Follow us on @ScimagoJR

EST MODUS IN REBUS
Horatio (Satire 1,1,106)

Edit Cookie Consent

Journal of Physics: Condensed Matter

PAPER

Temperature dependence of the Young’s modulus of polymers calculated using a hybrid molecular mechanics–molecular dynamics method

To cite this article: Iwan H Sahputra *et al* 2018 *J. Phys.: Condens. Matter* **30** 355901

IOP Publishing Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **30** (2018) 355901 (6pp) https://doi.org/10.1088/1361-648X/aad588

Temperature dependence of the Young's modulus of polymers calculated using a hybrid molecular mechanics–molecular dynamics method

Iwan H Sahputra, Alessio Alexiadis and Michael J Adams

School of Chemical Engineering, University of Birmingham, Birmingham, United Kingdom

E-mail: I.H.Sahputra@bham.ac.uk

Received 19 June 2018, revised 19 July 2018
Accepted for publication 24 July 2018
Published 7 August 2018

Abstract

A hybrid molecular mechanics–molecular dynamics (MM–MD) method is proposed to calculate the Young's modulus of polymers at various temperature. It overcomes the limitation that MD is restricted to extremely high strain rates. A case study based on poly-methyl-methacrylate demonstrates that, contrary to previous MD studies, the method is able to accurately reproduce the effect of temperature on the Young's modulus in close agreement with experimental data. The method can also predict a more clear transition between the glassy and rubbery states than previous MD studies.

Keywords: Young's modulus, molecular mechanics, molecular dynamics, glass transition, poly-methyl-methacrylate

(Some figures may appear in colour only in the online journal)

1. Introduction

Molecular dynamics (MD) simulations have been increasingly utilised to study the behaviour of polymers and, in particular, to calculate their physical, chemical and mechanical properties. However, to study structural deformation under the influence of applied strain or stress (e.g. to calculate the Young's modulus) there are challenges in tracking the detailed evolution of the system over an experimental time-scale. The polymer chains are trapped in local energy minima and, hence, relatively long times are required to achieve the global minimum. This cannot be addressed by MD since the time-steps are of the order of femtoseconds. In MD, the integration of the equation of motion is performed sequentially and thus parallelization of processors does not reduce the computational time required.

Several methods have been proposed to accelerate MD simulations for such applications, e.g. by using higher temperatures, strain rates or stresses. However, greater values of these parameters affect the physical properties of organic polymers particularly during deformation, for example, higher strain rates increase the Young's modulus while higher temperatures lead to a reduction [1–3]. Moreover, the lowest strain rates that can be applied even with high performance computing is of the order of 10^7–10^9 s^{-1} so that even by increasing the temperature it is only possible to access mechanical properties in the glassy or near-glassy state. Thus, thermally induced transitions to the rubbery or melt states cannot be studied nor those induced by plasticisation. The current lowest strain rates that are accessible by MD are still much higher than experimental quasi-static loading rates, which are typically less than 10^{-1} s^{-1}.

Other approaches have been proposed to address the time-scale limitation of MD, for example, temperature-accelerated dynamics [4], parallel-replica dynamics [5], metadynamics [6] and hyperdynamics [7]. These methods have been developed primarily to investigate the behaviour of systems in the absence of externally applied stresses or strains, such as diffusion and chemical reactions. However, the computation of the Young's moduli depends normally on applying a small external strain and, consequently, these methods are unsuitable for this application.

An alternative strategy is the application of small incremental strains at a constant strain rate and subsequent relaxation of the system after each increment [8, 9]. However, in practice even the lower limit of the accessible strain rates is extremely high; therefore the system has only a very limited time to explore its potential energy surface (PES). As a result, there is a limit to the magnitude of the energy barriers that can be crossed and thus the system will adopt a meta-stable state corresponding to a local but not a global energy minimum. Other methods have been developed to mitigate this effect. The ABC (autonomous basin climbing) method [10, 11] is probably the most widely applied in which penalty functions are incorporated to the PES in order to drive the system out of the current energy level. The ABC approach is mainly used for metals [12–14], and has a number of disadvantages [15], e.g. (i) it is computationally expensive because of the penalty functions, (ii) there is not a rigorous approach for selecting the appropriate penalty functions and (iii) the method is more suitable at low temperatures when the entropic effects are not dominant, i.e. when the energy barriers are high such that the entropy can be neglected.

In the current work, a combination of molecular mechanics (MM), energy minimization and MD simulation is proposed to study the effect of temperature on the Young's modulus of polymers. MM is based on a model of atomic interactions within a system by considering related processes such stretching, deviations and rotations about single bonds. The arrangement of the atoms in the stable state corresponds to the minimum energy, which commonly is computed by the application of a minimization algorithm. The macroscopic properties then can be calculated from the stable configuration. However, the contribution of the kinetic energy to the dynamics of the system is ignored in MM, and consequently the effects of temperature are not considered. MD accounts for the dynamics in terms of both the potential and kinetic energies. Therefore, combining MM, energy minimization and MD will drive the system to the stable state at the specified temperature and then the macroscopic properties may be calculated much more accurately. Thus, this hybrid approach does not require penalty functions as is the case for the ABC method and is applicable to any temperature.

2. Methods

The procedure employed for combining MM and MD, as illustrated in figure 1, is listed below.

1. NVT step: initially the system is equilibrated at a specified temperature (NVT ensemble) by means of MD simulations.
2. MM step: a small strain increment is applied instantaneously in one orthogonal direction of the simulation box by changing the length of the box in that direction and re-mapping the atomic coordinates to the new box dimension. This will cause a deviation from the previous stable configuration to a new configuration with a greater potential energy level. In this MM step, only the potential energy is perturbed due to changes in the position of the atoms.

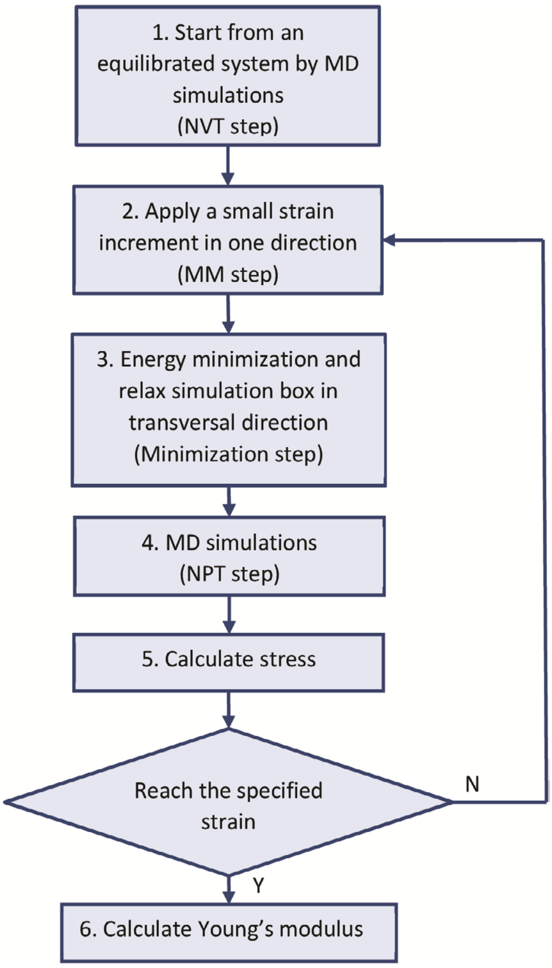


Figure 1. Flowchart of the hybrid MM-MD method to calculate the Young's modulus.

3. Minimization step: energy is minimized using a conjugate gradient algorithm while maintaining the value of the imposed strain. During minimization, the box size is changed in the transversal direction to maintain a constant external pressure of 1 atm. This is important for compressible materials, such as polymers, with Poisson's ratio < 0.5. To control the external pressure during energy minimization, a method proposed by Parrinello and Rahman [16] is employed, based on the objective function:

$$E = U + P_t (V - V_0) + E_{\text{strain}} \tag{1}$$

where U is the potential energy of the system, P_t is the target pressure, V and V_0 are the system and reference volumes, and E_{strain} is the strain energy expression proposed by Parrinello and Rahman.
4. NPT step: the minimization step minimizes the potential energy, but it does not control the temperature of the system. This is achieved in the current step, when the system is further evolved by means of MD simulation at

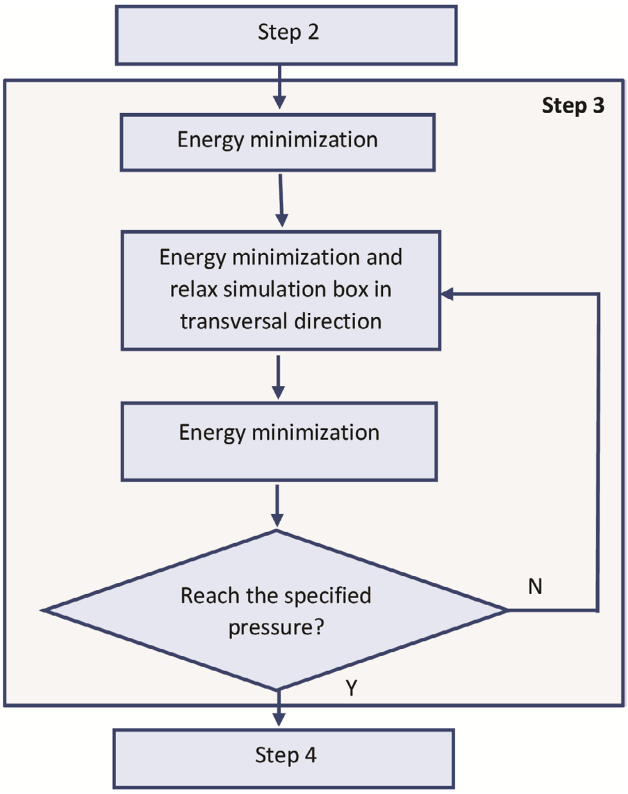


Figure 2. Step 3 may be combined with additional energy minimization processes and repeated several times in order to gradually change the pressure to the specified value.

the specified temperature and also 1 atm pressure in the transversal directions. This step will drive the system to the stable state such that it accounts for the contribution from both potential and kinetic energies.

5. Stress calculation step: finally, the stress, σ, is calculated taking account of the contribution from both the potential and kinetic energies by using the following expression:

$$\sigma = \frac{\sum_i^N m_i v_i^2}{V} + \frac{\sum_i^N r_i \cdot f_i}{V} \tag{2}$$

where N is the number of atoms in the system, m_i the mass of atom i, v_i the velocity of atom i, V the system volume, r_i the position of atom i, and f_i the force acting on atom i.

Steps 2–5 are repeated to calculate the stress for the range of imposed strain values.

6. Calculation of the Young's modulus: The Young's modulus is calculated from the linear gradient of the stress as a function of strain using the least squares best fit.

In step 3, the pressure defined by equation (1) is a sensitive function of the volume and, in order to achieve the objective pressure, the minimization algorithm changes the volume; thus it can be difficult for the algorithm to minimize the energy of the system at the specified pressure with high precision. Therefore, in some cases, it is required that step 3 in combination with additional minimization energy processes, is repeated several times in order to gradually change the pressure to the specified value (figure 2).

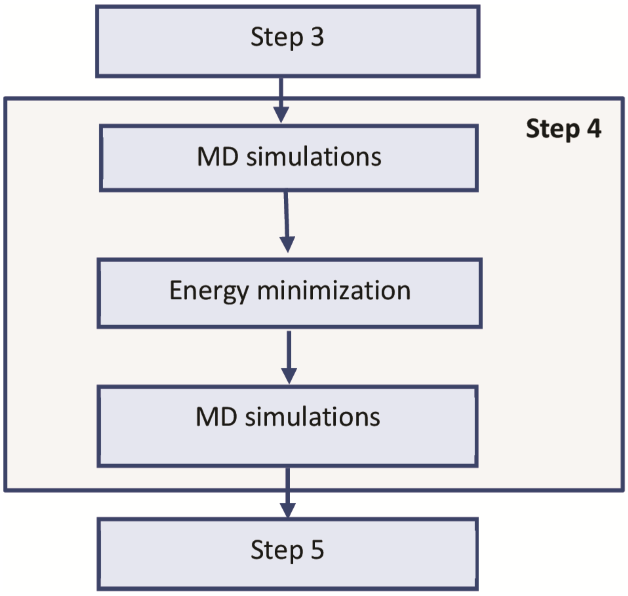


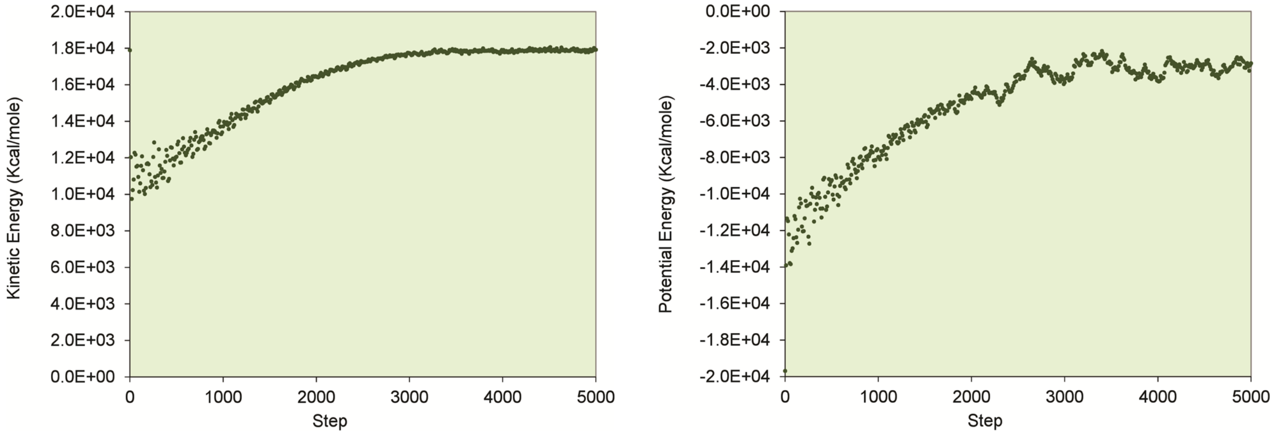
Figure 3. An energy minimization process may be performed in between two MD simulations in step 4 to accelerate the rate at which the equilibrium state is achieved.

In step 4, to increase the rate at which the stable state is achieved, an additional energy minimization process may be performed between MD simulations (figure 3). The fluctuation of the properties of the system, such as energy, temperature and pressure, are monitored until the values become stable. When equilibrium has been reached, the fluctuations are proportional to $1/\sqrt{N}$ where N is the size of the system.

3. Application of the MM-MD method: a case study for poly-methyl-methacrylate

In this section, the method is applied to the specific case of poly-methyl-methacrylate (PMMA). It is well established that increasing the temperature of a polymer reduces the elastic moduli e.g. the tensile storage modulus of PMMA [17, 18] (the storage modulus is approximately equal to the elastic modulus for a single, rapid stress at a small strain in the linear viscoelastic region [19]). The current case study involves an isotactic-PMMA model containing 5 chains, each with 400 monomers, and the DREIDING force field [20] was employed. The details on how to prepare and equilibrate the model are described in a previous publication [21], where the validity of the DREIDING force field was evaluated and compared to other force fields.

For each equilibrated model at a range of temperatures (200–400 K), the hybrid MM-MD method was applied to calculate the Young's modulus using LAMMPS [22]. The maximum strain was set to 1% for which a linear relationship between stress and strain is typically observed experimentally. The strain was applied by ten successive small strain increments (i.e. 0.1% strain increments each for step 2 in figure 1) in order to obtain sufficient data points for calculating the gradient. The Polak–Ribiere version [23] of the conjugate gradient algorithm was used for the energy minimization processes with a force stopping criteria of 10^{-9}. Steps 3 and 4



(a) (b)

Figure 4. Evolution of the kinetic energy (a) and potential energy (b) during the first 5000 MD simulation time-steps (step 4). The temperature decreases after the energy minimization in step 3 and the thermostat in the MD simulations of step 4 increases the temperature, and thus the kinetic energy.

were performed as those described in figures 2 and 3. The MD simulations were done with a time step of 1 fs.

Figure 4 shows an example of the implementation of the method using the model equilibrated at 200 K, during step 4—MD simulations. The temperature and pressure were controlled using the Nosé–Hoover thermostat and barostat. Initially, the temperature was calculated to be about 100 K. The lower temperature here is due to the previous energy minimization (step 3), where the temperature was not maintained at 200 K. After about 3000 time-steps of the simulations, the temperature increases to the specified value of 200 K. There was a corresponding increase in the kinetic energy (figure 4(a)) and a reduction (i.e. less negative value) in the potential energy (figure 4(b)). There is a linear relationship between the calculated stress and strain as shown in figure 5 and the Young's modulus was calculated from the gradient.

The computed effect of temperature on the Young's modulus is plotted in figure 6 together with the DMA experimental tensile storage modulus data [17] and previous MD simulation results [21, 24]. The DMA measurements were performed at a frequency of 1 Hz, which corresponds to a strain rate of 2.1×10^{-3} s^{-1}. The previous MD simulations were carried out with a full atom model at a constant strain rate of 10^9 s^{-1} and the Young's moduli were calculated from the gradients of the stress–strain curves [21], and also with a united atom model at a small deformation with the Young's moduli calculated from the stiffness matrix constants [24].

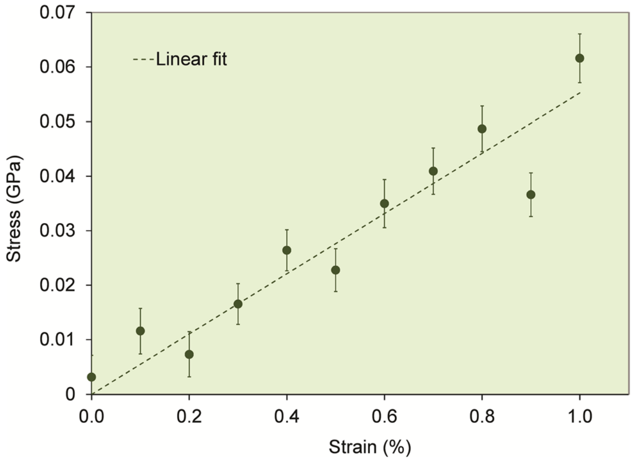


Figure 5. A plot of the stress as a function of strain calculated for the PMMA model at 200 K; the Young's modulus is calculated from the gradient of the best linear fit (dashed line).

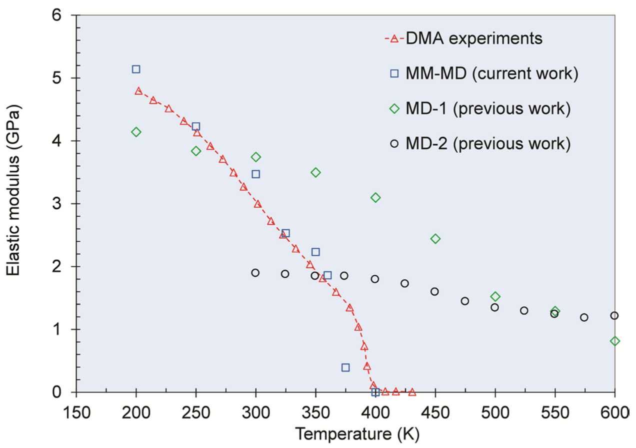


Figure 6. A comparison of the measured (DMA experiments [17]) and computed values of the Young's moduli as a function of temperature. The computed values correspond to those obtained in the current work (MM-MD) and previous MD results (MD-1 (previous work) [21] and MD-2 (previous work) [24]).

Figure 6 shows that MD alone (MD-1 and MD-2) does not result in a close fit to the experimental data, while the MM-MD technique proposed here achieves a very close agreement. The moduli calculated by simulations MD-1 are in a good agreement with the experimental values at temperatures in the range 200–300 K. However, the results are much greater than experimental values at temperatures > 300 K. On the other hand, the modulus calculated by simulations MD-2 is smaller at temperature 300 K, and the moduli are greater at temperatures > 375 K compared to the experimental values. The high strain rates associated with MD simulations (MD-1

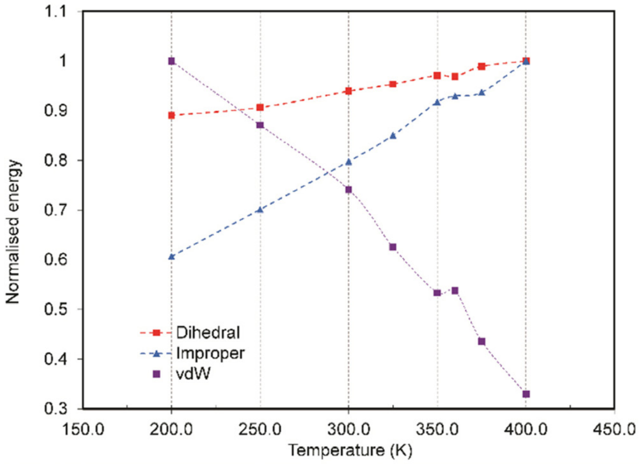


Figure 7. Normalised dihedral, improper and van der Waals (vdW) energies as a function of temperature. There is a change in the gradient at the temperature about 350 K, which is related to the Tg.

and MD-2) restrict the mobility of the polymer chains under uniaxial tension and the polymer has a glassy response even at temperatures greater than the glass transition value (Tg). Thus, it is not possible to study thermally induced transitions to the rubbery or melt states using the conventional MD simulations. However, the moduli calculated using the proposed method at various temperatures are in a close agreement with the experimental values, even at high temperatures. Thus, this method can be developed further to examine other temperature and rate dependent behaviour of viscoelastic materials, such as creep and stress relaxation. For example, it could be applied to examine the plasticisation of organic polymers that result in a transition from the glassy to the rubbery state.

The relatively close agreement between the calculated and the DMA measurement values shown in figure 6 suggests that the MM-MD method can achieve stable states of the system deformed with a strain rate equivalent to an experimental value of order 10^{-3} s^{-1}. Thus this method can be used to calculate the Young's modulus of polymers at a strain rate that is comparable to typical experimental quasi-static loading rates. With the current computation technology, the smallest strain rates that are accessible by conventional MD simulations are still much greater than those that can be achieved by the proposed method.

Figure 6 also demonstrates that the hybrid MM-MD method can be used to calculate, within a close approximation, the Tg of the polymer. It may be observed that there is a sharp decrease in the calculated and experimental Young's modulus for the temperature range of 350–400 K. This indicates a transition between the glassy and rubbery regions of PMMA. Previous MD studies (MD-1 and MD-2) could not effectively reproduce this transition. Simulations MD-1 produce only a slow decrease in the modulus in the temperature of range 400–500 K. Moreover, simulations MD-2 indicate only a small change in modulus at high temperatures. Therefore, it is difficult to predict the Tg by using conventional MD simulations.

Small discrepancies between the calculated Tg by using the proposed method and the experimental value may be caused by several factors, such as the differences in the tacticity, number of monomers, number of chains, and thermal history of the experimental samples and the simulation model. The Tg of PMMA has been shown experimentally to depend on the degree of polymerisation and tacticity [25] but is in the range 328–397 K. Additionally, the molecular weight of the current simulated PMMA is 40 kDa, which is greater than the critical entanglement value; it is considerably less than that of typical commercial PMMAs, which are in the range 130–2200 kDa [26]. The computational time required by the method is approximately a factor of 10 longer than previous work (MD-1) when performed using the same number of processors and the same high performance computing machine. Considering that the strain rate applied in the previous method (MD-1) is much faster (10^9 s^{-1}) compared with the proposed method (~10^{-3} s^{-1}), the computational time required by the method is still reasonable.

The glass transition behaviour is also shown in the other temperature dependence properties, such as specific volume or enthalpy, measured experimentally. Theoretically, the volume change and glass transition when polymers are cooled may be explained by the free volume concept; at the same temperature, a polymer with higher Tg has a lower percentage free volume than one with lower Tg [27]. The free volume is the volume which is not 'occupied' by polymers' molecules. The volume occupied by polymers' molecules depends on the arrangement of the polymer chains. In MD, some properties at atomistic level can be accessed and calculated to provide additional insights about the nature of the glass transition.

Figure 7 presents the normalised dihedral, improper and van der Waals (vdW) energies as a function of temperature calculated in step 4 (see figure 1). It may be observed that there is a transition in the gradient of the energies at a temperature of ~350 K, which is related to the Tg. The dihedral and improper energies are those required for rotation about a chemical bond and out-of-plane bending motions respectively, thus they affect the change in structure of individual polymer chains. These motions require less energy than stretching or bending bonds and therefore most variation in polymer structure arises from these motions. Higher dihedral and improper energies at a high temperature indicate that the structure has a larger free volume, providing more space for molecular vibrations. On other hand, the vdW energy depends on the interactions between different polymer chains, which is affected by the structure of individual chains and their neighbours. A greater vdW energy at a low temperature indicates a more compact structure of the polymer chains and thus less free volume, which restricts the movement of the chains sliding against each other.

4. Conclusion

A hybrid MM-MD method for calculating the temperature dependence of the Young's modulus for organic polymers has been developed. It overcomes the limitation of MD of being restricted to extremely high strain rates and thus not able to accurately account for thermal softening, which is observed at experimental accessible strain rates. Additionally, the method can be used to calculate the temperature of the glass-rubber transition within a close approximation.

Acknowledgments

This work was supported by the Engineering and Physical Sciences Research Council (grant number: EP/M02959X/1). The computations using the hybrid MM-MD method have been performed on the supercomputing system of the Institute of Process Engineering, Chinese Academy of Sciences.

ORCID iDs

Iwan H Sahputra https://orcid.org/0000-0001-9851-7646

References

[1] Arruda E M, Boyce M C and Jayachandran R 1995 Effects of strain rate, temperature and thermomechanical coupling on the finite strain deformation of glassy polymers *Mech. Mater.* **19** 193–212

[2] Nasraoui M *et al* 2012 Influence of strain rate, temperature and adiabatic heating on the mechanical behaviour of poly-methyl-methacrylate: experimental and modelling analyses *Mater. Des.* **37** 500–9

[3] Kendall M J and Siviour C R 2014 Experimentally simulating high-rate behaviour: rate and temperature effects in polycarbonate and PMMA *Phil. Trans. R. Soc.* **372** 20130202

[4] Sorensen M R and Voter A F 2000 Temperature-accelerated dynamics for simulation of infrequent events *J. Chem. Phys.* **112** 9599–606

[5] Perez D, Uberuaga B P and Voter A F 2015 The parallel replica dynamics method—coming of age *Comput. Mater. Sci.* **100** 90–103

[6] Laio A and Gervasio F L 2008 Metadynamics: a method to simulate rare events and reconstruct the free energy in biophysics, chemistry and material science *Rep. Prog. Phys.* **71** 126601

[7] Voter A F 1997 Hyperdynamics: accelerated molecular dynamics of infrequent events *Phys. Rev. Lett.* **78** 3908–11

[8] Cao P, Park H S and Lin X 2013 Strain-rate and temperature-driven transition in the shear transformation zone for two-dimensional amorphous solids *Phys. Rev.* E **88** 042404

[9] Cao P, Lin X and Park H S 2014 Strain-rate and temperature dependence of yield stress of amorphous solids via a self-learning metabasin escape algorithm *J. Mech. Phys. Solids* **68** 239–50

[10] Kushima A *et al* 2011 Time scale bridging in atomistic simulation of slow dynamics: viscous relaxation and defect activation *Eur. Phys. J.* B **82** 271

[11] Kushima A *et al* 2009 Computing the viscosity of supercooled liquids *J. Chem. Phys.* **130** 224504

[12] Fan Y *et al* 2013 Mapping strain rate dependence of dislocation-defect interactions by atomistic simulations *Proc. Natl Acad. Sci.* **110** 17756–61

[13] Yan X and Sharma P 2016 Time-scaling in atomistics and the rate-dependent mechanical behavior of nanostructures *Nano Lett.* **16** 3487–92

[14] Lau T T, Kushima A and Yip S 2010 Atomistic simulation of creep in a nanocrystal *Phys. Rev. Lett.* **104** 175501

[15] Xin Y *et al* 2016 Atomistic modeling at experimental strain rates and timescales *J. Phys. D: Appl. Phys.* **49** 493002

[16] Parrinello M and Rahman A 1981 Polymorphic transitions in single crystals: a new molecular dynamics method *J. Appl. Phys.* **52** 7182–90

[17] Mulliken A D and Boyce M C 2006 Mechanics of the rate-dependent elastic–plastic deformation of glassy polymers from low to high strain rates *Int. J. Solids Struct.* **43** 1331–56

[18] Richeton J *et al* 2005 A unified model for stiffness modulus of amorphous polymers across transition temperatures and strain rates *Polymer* **46** 8194–201

[19] ISO 6721 2011 *Plastics—Determination of Dynamic Mechanical Properties-Part 1: General Principles* (International Organization for Standardization)

[20] Mayo S L, Olafson B D and Goddard W A 1990 DREIDING: a generic force field for molecular simulations *J. Phys. Chem.* **94** 8897–909

[21] Sahputra I H, Alexiadis A and Adams M J 2018 Temperature and configurational effects on the Young's modulus of poly (methyl methacrylate): a molecular dynamics study comparing the DREIDING, AMBER and OPLS force fields *Mol. Simulat.* **44** 774–80

[22] Plimpton S 1995 Fast parallel algorithms for short-range molecular dynamics *J. Comput. Phys.* **117** 1–19

[23] Polak E and Ribiere G 1969 Note sur la convergence de méthodes de directions conjuguées *ESAIM- Math. Model. Num.* **3** 35–43

[24] Mohammadi M and Davoodi J 2017 The glass transition temperature of PMMA: a molecular dynamics study and comparison of various determination methods *Eur. Polym. J.* **91** 121–33

[25] Ute K, Miyatake N and Hatada K 1995 Glass transition temperature and melting temperature of uniform isotactic and syndiotactic poly(methyl methacrylate)s from 13mer to 50mer *Polymer* **36** 1415–9

[26] Wypych G 2016 *Handbook of Polymers* (Toronto: ChemTec Publishing)

[27] White R P and Lipson J E G 2016 Polymer free volume and its connection to the glass transition *Macromolecules* **49** 3987–4007