UNIVERSIDAD AUTÓNOMA DEL ESTADO DE MÉXICO

FACULTAD DE CIENCIAS

Protocolo de Tesis:

"Análisis Termodinámico de Clatratos de Etano"

Aspirante

Fís. Gustavo Torres García

Comité Tutorial

Dr. Jorge López Lemus (Tutor Académico)
Dr. Benjamín Ibarra Tandi (Tutor Académico)
Dr. Roberto López Rendón (Tutor Adjunto)

INTRODUCCIÓN

El gas natural se compone por metano, etano, propano, butano, entre otros, su principal componente es el metano seguido del etano. La formación de sólidos cristalinos depende de ciertas condiciones físicas. Cada tipo de clatrato tiene características cualitativas y cuantitativas particulares. El objeto de estudio en este trabajo son los **hidratos clatratos de etano**.

Los hidratos clatratos de gas se forman cuando existen las cantidades y condiciones adecuadas de gas, agua, temperatura y presión. Su formación se puede ver como un proceso de cristalización, se da cuando el agua y el gas entran en contacto comúnmente a presiones mayores a 0.1 MPa y temperaturas menores a 300 K. En el proceso de formación no se crean puentes de hidrógeno entre las moléculas de agua y gas, debido al efecto hidrófobo. La presión y la temperatura deben encontrarse en cierta región como lo muestra la figura 1.

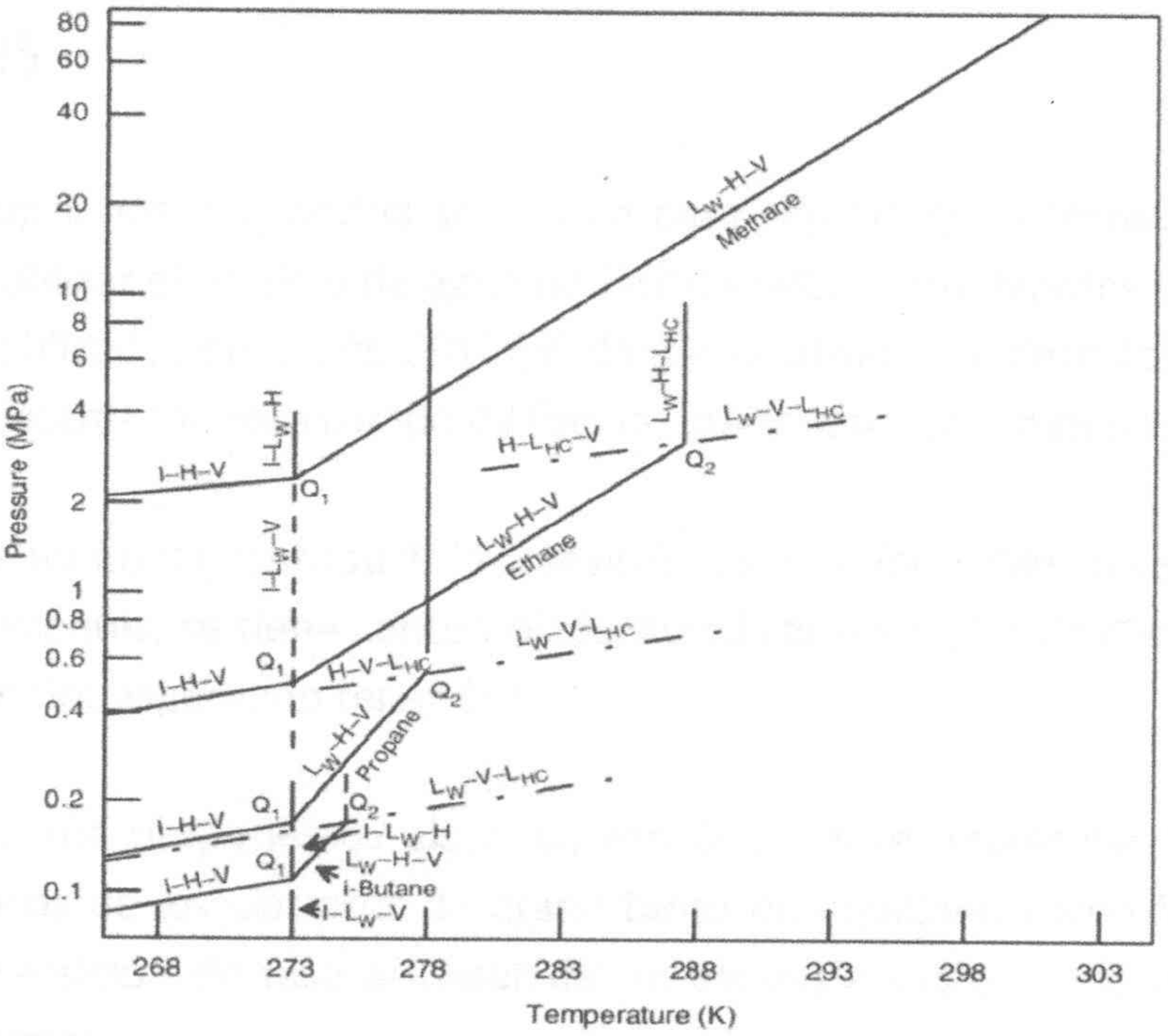


Figura 1. Diagrama de fase de cuatro tipos diferentes de clatratos de gas [1].

La estabilidad mecánica depende del tamaño de la molécula huésped. El objetivo se enfoca en reproducir a través de simulación molecular, ***la transición de los***

clatratos de etano al pasar de un estado termodinámicamente estable a otro termodinámicamente inestable.

Se calcularán diferentes tipos de propiedades estructurales esperando que diversos criterios de estabilidad puedan sustentar la transición estable-inestable, por mencionar algunos se alistan los siguientes: potencial de fuerza promedio, función de distribución radial, número de coordinación, energía potencial del sistema, puentes de hidrógeno y desplazamiento cuadrático promedio.

El estudio de los hidratos desde un contexto científico tiene una variedad relevante de aplicaciones, su campo incluye modelamiento del cambio climático [2], inhibición de los hidratos de gas [3], secuestración del dióxido de carbono [4], nucleación y crecimiento [5,6], biología marina [7], preservación de órganos [8], entre otras.

HIPOTESIS

Una de las opciones que podría ser viable para reproducir la transición estable-inestable es utilizar el modelo de agua de 3-sitios SPC/E, esta hipótesis se apoya en resultados publicados en el año 2010 [9] donde se observó la desestabilización del clatrato de metano con esta campo de fuerza, utilizando una temperatura de 270K.

En el caso de no lograr reproducir la transición estable-inestable con siete campos de fuerza diferentes, se tiene contemplado modificar las reglas de combinación de Lorentz-Berthelot esperando tener éxito.

Los objetivos que proponemos alcanzar, estudiar a nivel molecular los procesos termodinámicos de los clatratos de etano tanto en equilibrio como fuera de él y analizar la transición de fase al pasar de un estado estable a uno inestable, de manera concreta:

OBJETIVO GENERAL:

Estudiar y analizar mediante dinámica molecular la estructura y los procesos de transición de los clatratos de etano.

OBJETIVOS PARTICULARES:

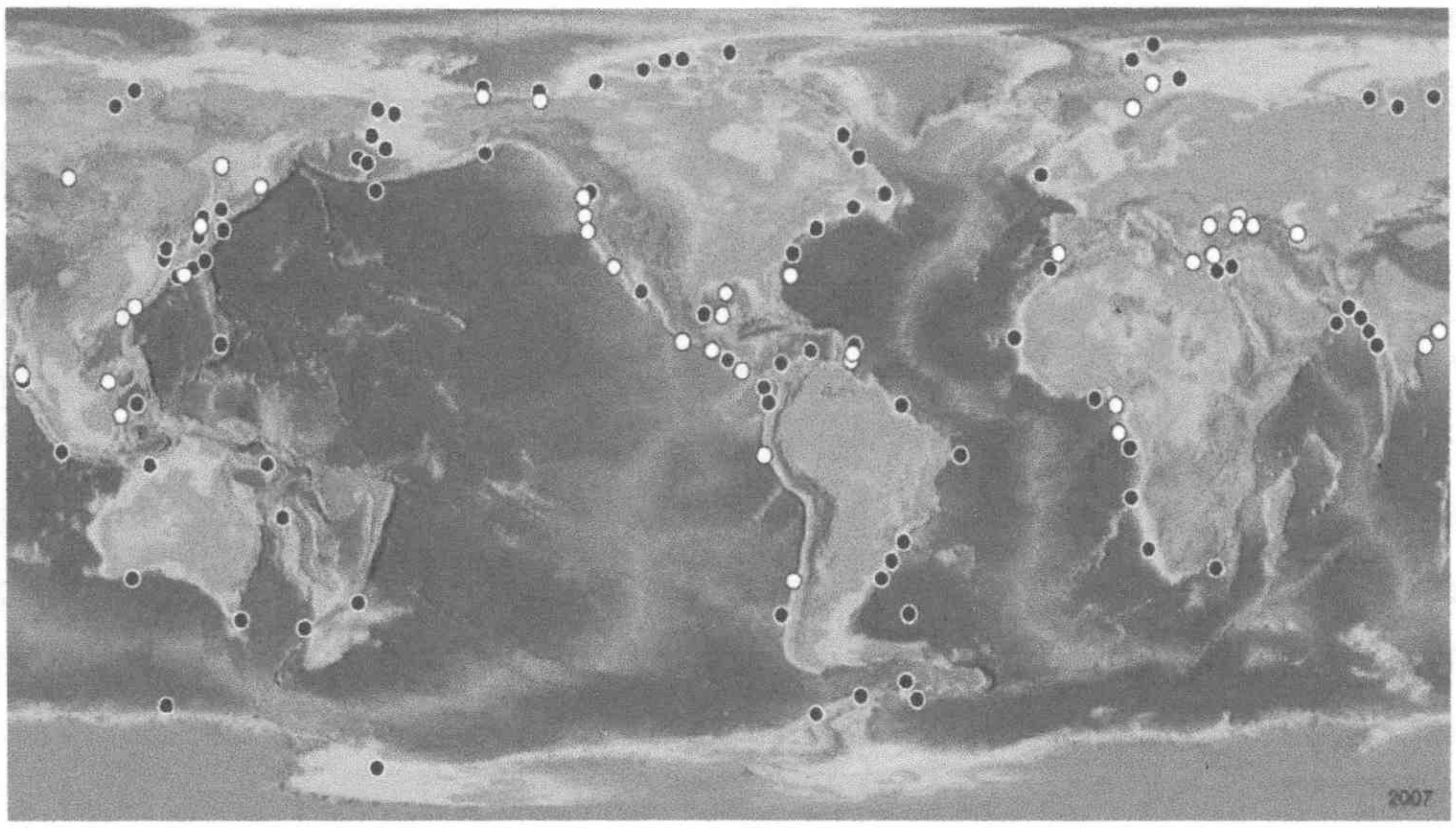
- Determinar qué modelo del agua reproduce la transición estable-inestable del clatrato de etano.
- Analizar mediante dinámica molecular la transición de fase de clatratos de etano al someterlos a la acción de una temperatura; el rango considerado es de 200 K hasta encontrar la desestabilización mecánica del sistema.

REVISIÓN BIBLIOGRÁFICA

A principios de 1930 la industria del gas natural comenzó a transportar este recurso a través de tuberías. Durante el proceso se observó que las líneas de conducción eran bloqueadas por tapones que se forman gradualmente [10]. Al hacer los estudios correspondientes a estas formaciones se identificaron como clatratos de gas. La prevención de la aglomeración de hidratos en las tuberías es el principal reto industrial. Ocurre en ambientes hostiles como el ártico donde la temperatura es muy baja y en gasoductos submarinos donde la presión puede llegar a niveles muy elevados.

Figura 1. Tapón formado por clatratos de gas en una línea de conducción, cortesía de Petrobras.

Por otro lado, se sabe que el petróleo, el gas y el carbón son una fuente de energía no renovable. Estas fuentes de energía son finitas y tarde o temprano se acabarán, por lo que es necesario buscar nuevas fuentes de energía. Una de estas se encuentra en los hidratos clatratos de gas que se hallan en el fondo marino y en regiones polares [11,12]. Se estima que el gas natural enclaustrado en los hidratos superan el doble de todos los depósitos de combustibles fósiles combinados que hay en la tierra [13,14,15].



METODOLOGÍA GENERAL

En la actualidad existen diferentes métodos de simulación molecular para estudiar sistemas en equilibrio térmico. El sistema simulado compuesto por clatratos de etano desde una perspectiva termodinámica se puede ver como un proceso irreversible.

Como ya se mencionó, el sistema que nos interesa estudiar está compuesto por una red de moléculas de agua que encapsulan a las moléculas de etano y que se encuentran a baja temperatura y alta presión.

Se llevarán a cabo simulaciones a nivel molecular mediante dinámica molecular. Planeamos simular el agua mediante los modelos rígidos SPC, SPC/E, TIP4P, TIP4Q, TIP4P/2005, TIP4P/ICE y TIP5P; modelando a la molécula de etano con un modelo de dos sitios conocido como campo de fuerza NERD. En durante el desarrollo del trabajo se propone analizar y observar los cambios significantes en la estructura del clatrato de etano con diversos criterios como son: energía potencial, función de distribución radial. Mediante los potenciales de Lennard-Jones y Coulomb vamos a modelar las interacciones iónicas y de Van der Waals. Para aumentar la eficiencia del cálculo de la contribución electrostática a la energía potencial aplicaremos la metodología llamada Particle Mesh Ewald (PME).

CRONOGRAMA DE ACTIVIDADES

	1er año											
Actividad	**1mes**	**2mes**	**3mes**	**4mes**	**5mes**	**6mes**	**7mes**	**8mes**	**9mes**	**10mes**	**11mes**	**12mes**
Revisión Bibliográfica	X	X	X	X	X							
Desarrollar el código de simulación molecular					X	X	X	X	X			
Reproducir datos experimentales para el etano y el agua								X	X	X	X	X
Pruebas y correcciones									X	X	X	
Producción de datos de los clatratos de etano									X	X	X	X
Unidades de aprendizaje	X	X	X	X	X	X	X	X	X	X	X	X

	2do año											
Actividad	**1mes**	**2mes**	**3mes**	**4mes**	**5mes**	**6mes**	**7mes**	**8mes**	**9mes**	**10mes**	**11mes**	**12mes**
Estadísticos y discusión de resultados	X	X	X	X	X	X						
Escritura del primer manuscrito				X	X	X	X	X				
Escritura y defensa de la tesis									X	X	X	X
Unidades de aprendizaje	X	X	X	X	X	X	X	X	X	X	X	X

BIBLIOGRAFIA

[1] E . Dendy Sloan and Carolyn A . Koh. *Clathrate Hydrates of Natural Gases, 3rd ed.* CRC Press, 2007.

[2] John Bohannon. Weighing the climate risks of an untapped fossil fuel. *Science*, 319(5871):1753, 2008.

[3] Minjun Cha, Kyuchul Shin, Yutaek Seo, Ju-Young Shin, and Seong-Pil Kang. Catastrophic growth of gas hydrates in the presence of kinetic hydrate inhibitors. *The Journal of Physical Chemistry A*, 117(51):13988–13995, 2013.

[4] Kranthi K. Godishala, Jitendra S. Sangwai, Nagham A. Sami, and Kousik Das. Phase stability of semiclathrate hydrates of carbon dioxide in synthetic sea water. *Journal of Chemical & Engineering Data*, 58(4):1062–1067, 2013.

[5] Matthew R. Walsh, Carolyn A. Koh, E. Dendy Sloan, Amadeu K. Sum, and David T. Wu. Microsecond simulations of spontaneous methane hydrate nucleation and growth. *Science*, 326(5956):1095–1098, 2009.

[6] Andrew H. Nguyen, Liam C. Jacobson, and Valeria Molinero. Structure of the clathrate/solution interface and mechanism of cross-nucleation of clathrate hydrates. *The Journal of Physical Chemistry C*, 116(37):19828–19838, 2012.

[7] C. R. Fisher, I. R. MacDonald, R. Sassen, C. M. Young, S. A. Macko, S. Hourdez, R. S. Carney, S. Joye, and E. McMullin. Methane ice worms: Hesiocaeca methanicola colonizing fossil fuel reserves. *Naturwissenschaften*, 87(4):184–187, 2000.

[8] T. Kin, T. Nemoto, K. Makino, and K. Koide. Molecular dynamics simulation of complex phase transition of clathrate hydrates in living body. In *Innovative Computing, Information and Control, 2006. ICICIC '06. First International Conference on*, volume 3, pages 556–559, Aug 2006.

[9] D.P. Luis, J. López-Lemus, M. Mayorga, and L. Romero-Salazar. Performance of rigid water models in the phase transition of clathrates†. *Molecular Simulation*, 36(1):35–40, 2010.

[10] E. G. Hammerschmidt. Formation of gas hydrates in natural gas transmission lines. *Industrial & Engineering Chemistry*, 26(8):851–855, 1934.

[11] Matthew R. Walsh, Steve H. Hancock, Scott J. Wilson, Shirish L. Patil, George J. Moridis, Ray Boswell, Timothy S. Collett, Carolyn A. Koh, and E. Dendy Sloan. Preliminary report on the commercial viability of gas production from natural gas hydrates. *Energy Economics*, 31(5):815–823, 2009.

[12] R Boswell. Is gas hydrate energy within reach? *Science*, 325(5943):957–958, 2009.

[13] Sloan E. Dendy. Fundamental principles and applications of natural gas hydrates. *Nature*, 426(6964):353–363, 2003.

[14] Imen Chatti, Anthony Delahaye, Laurence Fournaison, and Jean-Pierre Petitet. Benefits and drawbacks of clathrate hydrates: a review of their areas of interest. *Energy Conversion and Management*, 46(9–10):1333 – 1343, 2005.

[15] G. J. Moridis, T. S. Collett, M. Pooladi-Darvish, S. Hancock, C. Santamarina, R. Boswel, T. Kneafsey, Rutqvist J., kowalsky M. B., and T. M. Reagan. Challenges, uncertainties and issues facing

gas production from gas hydrate deposits. *SPE Reservoir Evaluation & Engineering*, 14:76–112, 2011.

Asunto: JCP: Receipt of New Manuscript MS #A15.07.0045

De: jcp-edoffice@aip.org (jcp-edoffice@aip.org)

Para: tavo_gtg@yahoo.com.mx;

Fecha: Viernes, 3 de julio, 2015 14:31:37

Dear Mr. Torres-Garcia,

On 03-Jul-2015, we received the manuscript entitled: "Decomposition of ethane clathrates using different water-ethane models: molecular dynamics".
Your manuscript is assigned the Manuscript #A15.07.0045.

We are sending you this notification because you are listed as one of the authors. If you as a coauthor do not approve its submission, please let us know as soon as possible by replying to this message. Refer to the manuscript number listed above in any correspondence. We would be happy to provide a copy of the paper for your information immediately. Otherwise, the manuscript has been cleared for editor assignment.

The order of the authors on your submitted manuscript is as follows: Gustavo Torres-Garcia, Daniel Luis-Jimenez, Gerardo Odriozola, and Jorge López-Lemus.
Please note that if this order is changed or if there are any deletions or additions of authors, each author must provide approval for this change.

Open Researcher and Contributor Identifier (ORCID):
Our records show that your account in our journal's peer review system is not currently associated with an ORCID ID. Please use the link below to either register for a new ORCID ID or, if you already have one, to login into the ORCID system and retrieve it. Your account in the journal's peer review system will then be associated with your ORCID ID, helping to correctly identify you.

http://jcp.peerx-press.org/cgi-bin
/main.plex?el=A6BK6EoEc5A2FlpK4Bh6B9ftdji6pmauUJuxodHXur7I9LAY The Open Researcher and Contributor Identifier (ORCID) connects research and researchers. ORCID provides a registry of unique identifiers that is open, non-proprietary, transparent, mobile, and community-based. To help the scientific community, we encourage all authors and reviewers to create and link an ORCID identifier to their account. For more information about ORCID, please visit http://orcid.org/content/about-orcid.

You may check on the status of this manuscript by selecting the "Check Manuscript Status" link at the following URL:

http://jcp.peerx-press.org/cgi-bin
/main.plex?el=A4BK7EoEc5A5FlpK6F2A9ftdhm01NsYLH2WJ0h9dknA4HQY
Thank you for submitting your work to The Journal of Chemical Physics.

Sincerely,

Editorial Office Staff
The Journal of Chemical Physics

Sincerely yours,

Editorial Office Staff
The Journal of Chemical Physics

** Impact factor is now 3.122 and still the most highly cited journal in Atomic, Molecular & Chemical Physics.**

Return to Main Page | **Help/Feedback** | **Log Out**

AIP | The Journal of Chemical Physics

About the Journal | **Information for Authors** | **General Editorial Policies** | **Author Instructions for Using This Site** | **Contact Editorial Office**

Manuscript #	A15.07.0045
Current Revision #	0
Submission Date	03-Jul-2015 14:35:35 **Days Since Original Submission: 4**
Current Stage	Securing Reviewer(s)
Title	Decomposition of ethane clathrates using different water-ethane models: molecular dynamics
Manuscript Type	49 - Article: Polymers and Soft Matter
Special Section	N/A
Corresponding Author	Jorge López-Lemus (Universidad Autonoma del Estado de México)
Contributing Authors	Gustavo Torres-Garcia , Daniel Luis-Jimenez , Gerardo Odriozola , Jorge López-Lemus (corr-auth)
Abstract	Decomposition of ethane clathrates is studied by means of molecular dynamics simulations in an isothermal-isobaric ensemble. For this purpose a temperature window of [200-440] K and a pressure of 2 MPa is considered. Structural analysis of the ethane clathrates is carried out at 200 K, where clathrates are stable for all considered models. It is found that structural properties of all stable clathrates do not strongly depend on the water model. Then, temperature is increased upon the clathrate turns unstable. This decomposition temperature is found by following coordination numbers, total number of hydrogen-bonds, potential energy, and mean-square displacements. All properties consistently point out the same temperature at which the stable-unstable transition takes place. For all water models and by using the standard combining rules, the obtained temperature at which the clathrate becomes unstable is higher than the experimental reference value. We have found that a reasonable way to approach the experimental decomposition temperature is by including a rescaling factor in the combining rules in such a way to decrease both, methyl-oxygen size and interaction energy. Our data point out that the decomposition temperature is much more sensitive to the methyl-oxygen size than to the potential well depth, suggesting that the entropic contribution is key to the clathrate stability.
Associate Editor	Assigned
Author Suggested Reviewers to Include	Juan Beltran (Royal Military College of Canada), Sanehiro Muromachi (AIST), Niall English (University College Dublin), Humberto Saint-Martin (UNAM)
Author Suggested Reviewers to Exclude	N/A
Keywords	Ethane Clathrates, Molecular Dynamics, structural analysis, Combining rules

Applicable Funding Sources	Cátedra CONACyT program ⚠ Proyect sabbatical/206693 ⚠ : 206693 CONACyT for supporting his M.Sc studies ⚠ Mainly, our funding sources come from CONACyT (National Council for Science and Technology-Mexico). The student GTG has a scholarship from CONACyT. JLL was supported by CONACyT for a sabbatical DPL has a position supported by CONACyT (Catedra Patrimonial)
Manuscript Significance	A structural analysis was done for ethane clathrates, performing molecular simulations. As a relevant result, we shown that the combining rules need to be modified in order to reproduce the experimental evidence. It was shown that the cross interaction between water and ethane molecules is the key issue in this analysis. Our data point out that the decomposition temperature is much more sensitive to the methyl-oxygen size than to the potential well depth, suggesting that the entropic contribution is key to the clathrate stability. We believe that using a convenient water model and suitable combining rules allow us to predict the decomposition of this kind of crystalline compound when they are under the effect of an external electric field or glycol for instance.
Figure/Table Permissions	Has a figure or table been reused from another source? No
Electronic Forms	1 of 1 forms complete - Jorge López-Lemus (Corr): ViewMs:MsDetails:Eforms:DetailedInfo:completed_message

Manuscript Items

1. Author Cover Letter (last updated: 07/03/2015 11:21:58) PDF (33KB)
2. Article File (last updated: 07/03/2015 13:30:18) PDF (787KB)

More Manuscript Info and Tools

Send Manuscript Correspondence

Check Status

Please view and update your Profile information regularly (use the General Task link on the Main Page)

Please review the Peer X-Press Privacy Policy

For proper operation of the service, please set your browser to accept cookies, to enable JavaScript, and to use Acrobat Reader

Visit JCP Online | Copyright transfer agreement | Publication Charge Information | Check Production Status of Accepted Manuscripts

1305 Walt Whitman Road, Suite 300, Melville, NY 11747-4300 USA

ECopyright Form -- AIP Publishing LLC

Journal : The Journal of Chemical Physics
Manuscript # :
Title : Decomposition of ethane clathrates using different water-ethane models: molecular dynamics
Authors : Gustavo Torres-Garcia, Daniel Luis-Jimenez, Gerardo Odriozola, and Jorge López-Lemus
Agreement Date : 03-Jul-2015 15:45 GMT

Please read this information carefully and select the appropriate copyright type for your work. You may choose only **one** copyright type, depending on whether you selected Open Access during submission:

- **Regular Publication / Not Open Access** - You must read the Transfer of Copyright Agreement below and select the correct copyright type based on your employment status.

- **Author Select / Open Access** - Only Creative Commons Attribution 3.0 Unported License (CC-BY) can be selected.

In both cases, you must agree to your choice and enter your signature in the text box to indicate your consent at the bottom of the form.

Regular Publication / *Not* Open Access *(If you seleced Open Access during submission, **SKIP** to the Author Select / Open Access section below.)*

Please read the AIP Publishing LLC Transfer of Copyright Agreement and select the correct copyright type.

Transfer of Copyright Agreement

Copyright to the above-listed unpublished and original article and subsequent, if necessary, errata, and the abstract forming part thereof submitted by the above author(s) (collectively, the "Article"), is hereby transferred to the AIP Publishing LLC for the full term thereof throughout the world, subject to the Author Rights (as hereinafter defined) and to acceptance of the Article for publication in a journal or conference proceedings of AIP Publishing LLC. This transfer of copyright includes all material to be published as part of the Article (in any medium), including but not limited to tables, figures, graphs, movies, and other multimedia files. AIP Publishing LLC shall have the right to register copyright to the Article in its name as claimant, whether separately or as part of the journal or conference proceedings or other medium in which the Article is included.

The author(s), and in the case of a Work Made For Hire, as defined in the U.S. Copyright Act, 17 U.S.C. § 101, the employer named below, shall have the following rights (the "Author Rights"):

1. All proprietary rights other than copyright, such as patent rights.

2. The nonexclusive right, after publication by AIP Publishing LLC, to give permission to third parties to republish the Article or a translation thereof, or excerpts therefrom, without obtaining permission from AIP Publishing LLC, provided the AIP Publishing LLC-formatted version is not used for this purpose and provided the Article is not to be published in another conference proceedings or journal. If the AIP Publishing LLC version is used, permission from AIP Publishing LLC must be obtained.

3. The right, after publication by AIP Publishing LLC, to use all or part of the Article without revision or modification, including the AIP Publishing LLC-formatted version, in compilations or other publications of the author(s)' and/or the employer's own works, including the author(s)' and/or the employer's web home page, and to make copies of all or part of the Article for the author(s)' and/or the employer's use for lecture or classroom purposes.

4. The right to post and update the Article on e-print servers as long as files prepared and/or formatted by AIP Publishing LLC or its vendors are not used for that purpose. Any such posting made or updated after acceptance of the Article for publication shall include a link to the online abstract in the AIP Publishing LLC journal or conference proceedings volume or to the journal or conference proceedings volume home page.

5. If the Article was prepared under a U.S. Government contract, the government shall have the rights under the copyright to the extent required by the contract.

All copies of the Article made under any of the Author Rights shall include notice of the AIP Publishing LLC copyright.

By signing this Agreement, the author(s), and in the case of a Work Made For Hire, the employer, jointly and severally represent and warrant that the Article is original with the author(s) and does not infringe any copyright or violate any other right of any third parties, and that the Article has not been published elsewhere, and is not being considered for publication elsewhere in any form, except as provided herein. If each author's signature does not appear below, the signing author(s) represent that they sign this Agreement as authorized agents for and on behalf of all the authors, and that this Agreement and authorization is made on behalf of all the authors. The signing author(s) (and, in the case of a Work Made For Hire, the signing employer) also represent and warrant that they have the full power to enter into this Agreement and to make the grants contained herein.

Click to see the list of Government Institutions

Please select a Copyright Type:

● **Regular** - I represent and warrant that I am (i) the sole author; (ii) the authorized agent to sign on behalf of all of the authors; (iii) the authorized agent to sign on behalf of the commissioning person or organization: or (iv) the authorized agent to s ign on behalf of my employer;

○ **U.S. Government** - I represent and warrant that all the author(s) prepared this work as part of official duties with the U.S . Government and therefore the work is not subject to copyright;

○ **U.S. Government-funded** - I represent and warrant that this work was prepared in the scope of my employment at a laboratory that receives U.S. Government funding and i) I am an authorized agent to sign on behalf of my employer; or ii) I am not authorized to sign on behalf of my employer but will supply an alternate form;

○ **United Kingdom Crown Copyright** - The work is subject to Crown Copyright. I am submitting a license agreement for AIP Publishing LLCs execution (Must be uploaded as an Alternate Copyright Form during Submission or Revision Stages Only);

○ **Canadian Crown Copyright** - The work is subject to Crown Copyright. I represent and warrant that I have received authorization to publish the work from the Crown Copyright and Licensing Section of Government of Canada Publishing. I am submitting a license agreement for AIP Publishing LLCs execution (Must be uploaded as an Alternate Copyright Form during Submission or Revision stages only);

○ **Australian Crown Copyright** - The work is subject to Crown Copyright. I represent and warrant that I have received authorization to publish the work from the Australian Commonwealth Department or other agency responsible for the work. I am submitting a license agreement for AIP Publishing LLCs execution. (Must be uploaded as an Alternate Copyright Form during Submission or Revision Stages Only);

○ **Euratom Agreement** - For use by The European Atomic Energy Community organizations. (Must be uploaded as an Alternate Copyright Form during Submission or Revision Stages Only);

Author Select / Open Access *(for Open Access only)*

○ **Creative Commons Attribution 3.0 Unported License (CC-BY) -** By choosing Author Select/Open Access you understand and agree that you must pay the open-access fee of $2200 prior to publication of your article. You will retain copyright but must agree to apply the Creative Commons Attribution 3.0 Unported License (CC-BY) to your work. The CC-BY license applies only in the case of open access and cannot be chosen in conjunction with Regular Publication or without the payment of the open-access fee.

Authors choosing Author Select/Open Access also grant AIP Publishing a license to publish the article and to be acknowledged as the publisher of record (original publisher) of the work. In granting this license to AIP Publishing the authors also represent and warrant that the article is original and does not infringe any copyright or violate any other right of any third parties.

Acting in the above capacity, you agree that in consideration of acceptance of the work for publication, you do hereby either agree to pay the fees associated with making your work Open Access, or you assign and transfer to the AIP Publishing LLC all the rights and interest in and to the copyright rights of the electronically attached/submitted work as specified in the AIP Publishing LLC Transfer of Copyright Agreement above, which you have read.

Please check one of the checkboxes below:

☑ **I accept this form in accordance with the form of publication and copyright type that I have chosen.**

☐ **I am unable to accept this form and an alternate copyright file has been uploaded.**

Please type your FULL First and Last Names (no initials) in the boxes below.

First Name: Jorge Last Name: Lopez-Lemus

You must provide assent to either the Author Select/Open Access option or the Transfer of Copyright Agreement, or provide an appropriate alternate form, in order for the AIP Publishing LLC to publish your paper. Send requests for further information to the Office of Rights and Permissions, AIP Publishing LLC, Suite 300, 1305 Walt Whitman Road, Melville, NY 11747-4300, USA; Phone: 516-576-2268; Fax: 516-576-2450; Email: rights@aip.org.

Please review your selection and make any changes, if necessary, before submitting this form.

local_p_id: 552121
time: 1435938472
ip address: 148.215.78.128

Return to Main Page | Help/Feedback | Log Out

AIP | The Journal of Chemical Physics

About the Journal | Information for Authors | General Editorial Policies | Author Instructions for Using This Site | Contact Editorial Office

Live Manuscripts

Tracking #	**Title**	**Days in Folder**
A15.07.0045	Decomposition of ethane clathrates using different water-ethane models: molecular dynamics	0

Please view and update your Profile information regularly (use the General Task link on the Main Page)

Please review the Peer X-Press Privacy Policy

For proper operation of the service, please set your browser to accept cookies, to enable JavaScript, and to use Acrobat Reader

Visit JCP Online | Copyright transfer agreement | Publication Charge Information | Check Production Status of Accepted Manuscripts

1305 Walt Whitman Road, Suite 300, Melville, NY 11747-4300 USA

Decomposition of ethane clathrates using different water-ethane models: molecular dynamics

Gustavo Torres-García[a], Daniel Porfirio Luis[b], Gerardo Odriozola[c] and Jorge López-Lemus[d*1]

[a]Facultad de Ciencias, Universidad Autónoma del Estado de México, Toluca, CP 50295, México.
[b]Centro de Ingeniería y Desarrollo Industrial, Querétaro, CP 76130, México.
[c]Área de Física de Procesos Irreversibles, División de Ciencias Básicas e Ingeniería, Universidad Autónoma Metropolitana-Azcapotzalco, D.F., CP 02200, México.
[d]Department of Chemistry, Imperial College London, SW7 2AZ, United Kingdom.

Abstract

Decomposition of ethane clathrates is studied by means of molecular dynamics simulations in an isothermal–isobaric ensemble. For this purpose a temperature window of [200–440] K and a pressure of 2 MPa is considered. Structural analysis of the ethane clathrates is carried out at 200 K, where clathrates are stable for all considered models. It is found that structural properties of all stable clathrates do not strongly depend on the water model. Then, temperature is increased upon the clathrate turns unstable. This decomposition temperature is found by following coordination numbers, total number of hydrogen-bonds, potential energy, and mean-square displacements. All properties consistently point out the same temperature at which the stable-unstable transition takes place. For all water models and by using the standard combining rules, the obtained temperature at which the clathrate becomes unstable is higher than the experimental reference value. We have found that a reasonable way to approach the experimental decomposition temperature is by including a rescaling factor in the combining rules in such a way to decrease both, methyl-oxygen size and interaction energy. Our data point out that the decomposition temperature is much more sensitive to the

---

[1] Permanent address: Facultad de Ciencias, Universidad Autónoma del Estado de México, Toluca, CP 50295, México.

*e-mail: jllemus@uaemex.mx

methyl-oxygen size than to the potential well depth, suggesting that the entropic contribution is key to the clathrate stability.

I Introduction

Natural gas hydrates are crystalline and nonstoichiometric compounds usually formed at low temperatures and high pressures. These crystalline arrangements are compounded by water and a nonpolar molecule. Most of the gas hydrates are classified into three structural groups, sI, sII, and sH [1, 2, 3, 4]. Typically, the type of the crystalline structure is determined by the guest-molecule size. Structure sI is observed for methane, ethane, and carbon dioxide among others. It consists on two pentagonal dodecahedron (5^{12}) cavities and six tetrakaidecahedron constituted by twelve pentagonal and two hexagonal faces ($5^{12}6^{2}$) [1]. Structures sII usually contain a small guest molecule, for example, hydrogen, oxygen, propane and nitrogen. This type of structure is formed by 16 dodecahedral 5^{12} cages and 8 hexakaidecahedral $5^{12}6^{4}$ cages [2]. The sH clathrate is formed with larger molecules either bromocyclopentane (BrCP) or bromocyclohexane (BrCH) [3, 5], as an example. As a difference with the previous structures, the sH clathrates consist on three types of cavities. It contains three 5^{12} cages, an icosahedron $5^{12}6^{8}$ cage, and two irregular dodecahedron cavities denoted as $4^{3}5^{6}6^{3}$, which means that it has three square faces, six pentagonal faces and three hexagonal faces [3, 4].

Gas hydrates impact on the energy industry. On the one hand, the study of gas hydrates is important because the vast reserves of natural gas hydrates represent an important energy source. The recovery of hydrocarbon from this source is, however, a complex challenge due to the risks of an environmental accident. On the other hand, there are other economic issues related to natural gas transport along the extracting and surface pipelines. Clathrates can appear inside the pipelines under suitable thermodynamic conditions which can impede the normal flow. Traditionally, some type of alcohol (*e.g.* methanol) is used to thermodynamically shift towards lower temperatures the clathrate formation to avoid blockage [6]. Other strategies involve a kinetic inhibitor.

Clathrates of small carbon molecules such as CH_4 and C_2H_6 conform sI structures [7]. In general, methane-hydrates have attracted more attention than ethane-hydrates. Nonetheless, there are important experimental contributions regarding the analysis of ethane clathrates and their mixtures with other small carbon molecules [11, 8, 9, 10]. Morita, Nakano and Ohgaki [12] have analyzed the stability of ethane hydrates, and among theirs findings, they report that the ethane molecules occupy all cavities in the sI structure. They also analyzed the stability dependency on pressure. Furthermore, the methane-ethane binary mixture has already been analyzed from an experimental point of view [7, 13], where several relative concentrations have been explored. Dec [14] analyzed the simultaneous formation of sI and sII structures for this same binary mixture. A study on the structural properties for the same kind of crystalline compounds have been performed by Erfan-Niya, Modarress and Zaminpayma [13], using molecular dynamics simulations.

The growing of carbon clathrates has been analyzed widely [15, 8], however, the decomposition of this same kind of crystalline compounds has not been extensively explored. Bishnoi and Natarajan [16] have pointed out that the hydrate decomposition is a sequence of structural arrangements and breakages, as well as the gas desorption processes. Some researches have also analyzed the CH_4 and C_2H_6 clathrates in a thermodynamic region where the crystalline compounds have been found forming a stable phase. Their studies focus on the understanding of the underlying mechanisms involved in the clathrate formation [4, 9, 10, 17]. It is useful to find out which water model is capable of matching the decomposition temperature of clathrates. This kind of study has already been performed for methane clathrates [18]. In this contribution the potential of mean force [19], PMF, and the coordination number were employed to capture the decomposition of such crystal structures. To the best of our knowledge, this kind of analysis has not been performed on ethane clathrates.

In this work we compare the structure of ethane clathrates by using different water models under stable thermodynamic conditions. This is done by means of molecular simulations in an isothermal–isobaric ensemble. Then, we examine the temperature at which the different systems destabilize and compare this value with the experimental one. For this purpose, structural and dynamical properties are employed for capturing the signature of a lack of stability of the crystalline compounds. We have found that all considered water models overestimate the decomposition temperature. This finding lead us to include a scaling factor on the combining rules for energy and distance. We find out that the decomposition temperature is sensitive to a decrease of the methyl-oxygen interaction size. The remainder of the manuscript is as follows: section II contains the simulation details. Results are shown and discussed in section III. Finally, conclusions are given in section IV.

II Methodology and simulation details

Different water models are considered for determining which one approaches the best the experimental temperature of decomposition (from a stable towards an unstable clathrate by crossing the phase transition line [4]). The water models are the following: the three sites models SPC [20] and SPC/E [21], the four sites models TIP4P [22], TIP4P/2005 [23], TIP4P/ICE [24], TIP4Q [25] and a model of five sites TIP5P [26]. The ethane model used in all simulations is the NERD model [27], which is constituted by two pseudoatoms (two methyl groups, $2CH_3$) bonded to each other. Both pseudoatoms contributes to the energy trough the Lennard-Jones potential. Most of the simulations were performed by using the Lorentz [28] and Berthelot [29] combining rules for estimating the cross interaction between different species. In addition, two extra series of simulations were carried out only for the SPC water model including a factor $\chi < 1$ in the mentioned combining rules. In one case,

the χ factor was included just in the Berthelot rule and in other case, the same factor was included in both geometrical and arithmetic rules for ϵ_{ij} and σ_{ij}, respectively.
These last two combining rules read as follows

$$\begin{aligned} \sigma_{ij} &= \frac{(\sigma_{ii} + \sigma_{jj})}{2} \\ \epsilon_{ij} &= \chi\sqrt{\epsilon_{ii}\epsilon_{jj}}, \end{aligned} \tag{1}$$

$$\begin{aligned} \sigma_{ij} &= \frac{\chi(\sigma_{ii} + \sigma_{jj})}{2} \\ \epsilon_{ij} &= \chi\sqrt{\epsilon_{ii}\epsilon_{jj}}, \end{aligned} \tag{2}$$

where σ_{ii} and ϵ_{ii} are the diameter and the attraction well depth between sites of the i species, respectively. χ equals unity in case of the original combining rules. As mentioned, for some of our simulations with the SPC water model χ is a fitting parameter to match the experimental temperature of decomposition. The standard Lorentz-Berthelot combining rules have been widely used for estimating the unlike dispersion interactions on different type of systems, in some works the effect of these combining rules on the thermodynamic properties of different types of mixtures has been reported [30, 31]. In some instances only one rule has been modified. e.g. for analyzing the excess chemical potential of methane in an aqueous electrolyte solution incorporating NaCl [32]. Despite the relevancy of this issue there are only a few contributions where the convenience of considering modified combining rules on clathrates hydrates is analyzed [34, 33, 35, 36]. In some of them only one rule is modified [34, 33], and in other instances both rules were modified [35, 36].

Molecular dynamic simulations are performed in an isothermal–isobaric ensemble. The free software Gromacs/4.5.5 [37, 38, 39, 40] is used to carry out the simulations. The leap-frog algorithm is employed to integrate the equations of motion, periodic boundary conditions were set and the minimum image convention was considered along the three spatial directions. The Berendsen barostat [41] and the Nosé-Hoover chain thermostats with 0.4 ps as time constants [42] are used to set pressure and temperature, respectively. The cut-off distance for the Lennard-Jones potential and for the real space contribution of the Coulomb potential is set to 1.2 nm. The long range Coulomb interaction is handled by the Particle Mesh Ewald method (PME)[43]. The time step in all our simulations is Δt=1 fs and all runs are carried out trough 20 ns. The LINear Constraint Solver (LINCS) [44] is used for handling constraints.

The initial configuration for ethane clathrates is taken from the experimental evidence supplied by McMullan and Jeffrey [45]. Although, the original array was settled for ethylene oxide hydrates, it provides the correct location of the water oxygens. In addition, the location

(CH_3–CH_3) and methyl–oxygen (CH_3–O) sites of all considered water models. The radial distribution functions for CH_3–CH_3 and CH_3–O were estimated at T=200 K and P=2 MPa. This temperature is far from the experimental critical temperature where the stable-unstable transition takes place, which at P=2 MPa is around T=285 K [4]. The standard Lorentz-Berthelot combining rules ($\chi = 1$) were used for these simulations.

Figure 1 shows the CH_3–CH_3 RDF's for all the considered water models at the same low temperature. The crystal-like structure is evident from the structured RDFs, which is build from localized CH_3 groups. As can be seen, all water models yield practically the same curves, pointing out a robust ethane clathrate hydrate structure which is insensitive to the employed water model. In fact, all water models produce a stable structure at these thermodynamic conditions. The average separation between first neighbors of pseudoatoms CH_3–CH_3 is, for all cases, around 0.61 nm. This distance can be compared to the one obtained for methane clathrates, which is 0.65 nm [18]. This indicates that the clathrate structure is practically independent of the size of the guest molecule. This small difference can be simply attributed to the fact that for methane its only site coincides with the geometric center of the molecule but this is not the case for ethane.

Figure 2 shows the CH_3–O RDF's in correspondence to Figure 1. that is to say, for the same simulations performed at T=200 K. This figure basically confirms the tiny dependence of the ethane clathrates on the employed water model. In all cases, the CH_3–O RDFs have a first peak at a distance around 0.38 nm. In this respect, it is worth mentioning that the only difference apprears for the SPC water case which shows a slightly lower first peak in comparison with the other cases. Again, this first peak distance can be compared with the one obtained for methane clathrates. This distance is 0.39 nm [18], confirming that the structure of this kind of clathrates is not sensitive to the size of the guess molecule. As in previous case, the smaller CH_3–O distance can be simply attributed to the guess geometry. On the other hand, our value compares well with the distance reported by Mancera *et al.* for T=279 K, 0.39 nm [17]. In this case the SPC water model and the NVE ensemble was employed. Figure 3 shows a snapshot of the ethane clathrate with the SPC water model.

An easy way to detect the destabilization of the structure is by means of the water coordination number of ethane molecules. This quantity is quite sensitive to the system structure. According to the experiment there are 25 oxygen atoms surrounding a carbon for the ethane clathrate structure [4] and it strongly drops for the liquid mixture. This number is plotted as a function of temperature in figure 4a. As always, this is done at 2 Mpa for all considered water models. The temperature was increased upon finding a sharp decrease of the coordination number, that is, a destabilization of the clathrate structure (this destabilization is confirmed by a snapshot visualization, structural analysis, and it strongly correlates with abrupt potential energy changes). This sharp drop of the coordination number can go from

25 oxygen atoms to 5 oxygen atoms for both SPC/E and TIP4P water models, and from 25 to 15 oxygen atoms for TIP4P/2005.

As shown in figure 4a, the temperature at which the destabilization occurs is strongly dependent on the employed water model. This contrast with the structural analysis performed at 200 K, where different water models lead to practically the same structure. Figure 4 also shows that the SPC, SPC/E, and TIP4P water models show the smallest decomposition temperatures. These models lead to decomposition temperatures inside the range [320–360] K. They all are, however, larger than the experimental value of 285 K. Indeed, the closer to the experimental decomposition temperature is obtained for the SPC water, i.e. 320 K. Actually, the SPC water model has been used in previous works regarding methane and carbon dioxide hydrates [50] and also for simulating ethane-methane clathrates [13]. The other water models lead to much larger decomposition temperatures. As an extreme case, the TIP4P/ICE water model yields the most stable system. Hence, none of the considered water models is able to reproduce the experimental value [4, 8]. This is despite the fact that the models for water and ethane molecules yield reasonable results as pure compounds [20, 21, 23, 27]. Hence, the mismatch of the decomposition temperature could be attributed to the water-ethane interaction. Other possible source for this mismatch lies on the fact that 20 ns cannot be compared with the experimental times. This can be important since the clathrate structure can persist in a metastable state before decomposing. Nonetheless, the relatively small simulation cells we are employing favor thermodynamic fluctuations which make easier to escape from local free energy minima. We did not observed our results to change significantly by performing larger simulations (up to 100 ns).

With the aim of approaching the experimental result we consider two modifications of the combination rules. We first have tried by only changing the Berthelot rule (by rescaling the energetic scale). This is done by including factor χ as a parameter for the methyl-oxygen interaction. A second test was then implemented by affecting both, ϵ_{ij} and σ_{ij}. That is, by rescaling energy and distance. This modifications were tested for the SPC water model, but similar results are expected for the other water models. The effect of varying χ on the ethane coordination number is shown in figure 4b. Here we are showing only the reference case (with the original rules, $\chi = 1$) and the two cases capable of reproducing the experimental value. These cases correspond to $\chi = 0.035$ when only the energy scale was rescaled, and to $\chi = 0.83$ when both combining rules are rescaled by this factor. Hence, to fit the experimental decomposition temperature a reduction of the ethane-water interaction is needed. Nonetheless, the decomposition temperature is much more sensitive to a decrease of the interaction distance (molecular size) than to a reduction of the energetic scale. This implies that the clathrate stability is much more dependent on the size of the guest than on its ability to strongly interact with the water cage. In other words, the guest stabilizes the clathrate by decreasing the water degrees of freedom, *i. e.*, by entropic reasons. In fact, a value of $\chi = 0.035$ cannot be justified while $\chi = 0.83$ seems much more reasonable. It is worth mentioning that combining rules are of empiric nature. Thus, it should not come as a surprise that for certain molecular pairs, such as a strong hydrogen-bonding dipole and a non-polar molecule, the rule leads to not so good results. Indeed, proposing modifications in combining rules is not a rare practice [33, 34, 51].

Another possible way to detect the destabilization of the clathrate structure is by means of the total number of hydrogen-bonds. We have included this number as a function of temperature in figure 5. This figure shows the same cases presented in figure 4. Here, symbols and colors are in correspondence with this figure. As expected, for all cases the number of hydrogen-bonds decreases with increasing temperature. This decrease is not very pronounced in the temperature window where the clathrates are stable, though. Once the clathrates decompose to form a liquid-like mixture there appear a sharp decrease. These drops are strongly correlated with the drops observed for the coordination number of ethane molecules. Thus, both quantities are good global parameters for detecting the decomposition of the clathrate structure. Conclusions from these data are, thus, identical to those already given in previous paragraphs.

Given a temperature at which the clathrate is not the stable phase, it is possible to measure the time at which the structure breaks down. The average of this breaking time over a large number of runs is related to the free-energy height which is a barrier that the system must overcome to reach the stable phase. In this case, the overall lowering of free energy is accompanied with an increase of the potential energy (the price is over-payed with an entropy gain). This potential energy gain is abrupt and easy to detect and points out that a structural change has taken place [34]. This is shown in figure 6a for some selected cases. These are for the SPC water at 285 K, for $\chi = 1$, $\chi = 0.035$ (only affecting the energy scale) and $\chi = 0.83$ (affecting both, energy and distance). We have also included the case for $\chi = 1$ and T=330 K. It is observed an invariant potential energy in the low temperature case for $\chi = 1$. This simply means that no decomposition of the clathrate was observed when using standard Lorentz-Berthelot combining rules. The cases where the combining rules were affected, do show a dramatic increase of the potential energy denoting a structural change of the system. For the case where only ϵ_{ij} was affected the increase is of 2000 KJ/mol. In the other case, the increase is close to 2500 KJ/mol. Note that the potential energy of the clathrate structure is similar for cases with $\chi = 1$ and $\chi = 0.83$, but case with $\chi = 0.035$ leads to a larger potential energy. This confirms that case with $\chi = 0.035$ cannot be supported. We are also including the case for $\chi = 1$ at T=330 K. This last case also leads to destabilization and to an increase of potential energy close to 2500 KJ/mol.

We have performed some extra computer simulations by using the force field OPLS/AA [52] for ethane molecules, which explicitly considers all hydrogen atoms. This was done to explore the possibility of detecting a shift of the decomposition temperature. In this case we have set $\chi = 0.83$ for both combining rules and T=285 K (P is always kept at 2 MPa). The result was a flat potential energy pointing out a stable clathrate. This is shown in figure 6b. Increasing T upon T=330 K does not produce any sign of destabilization. Only the simulation performed at T=340 K leads to a destabilization. Thus, there is an important shift of the decomposition temperature towards larger values, implying a more stable clathrate structure, by using the OPLS/AA for ethane molecules. Hence, explicit hydrogens do not supply any improvement. A structural change at T=340 K is far away from the temperature vicinity at which the experimental system loses stability.

The structural breakup from a crystal-like towards a liquid-like phase, can be also observed from the RDF's. In particular, we are showing in figure 7 the CH_3–CH_3 RDF's for the SPC water model with $\chi = 1$, as a function of the temperature. The loose of stability of the clathrate is obvious at T=330 K, in correspondence with strong changes of potential energy, number of hydrogen bonds, and water coordination numbers of ethane molecules. Similar conclusions can be drawn from figure 8. Here we are showing 4 panels for the SCP water model. Panel a) shows the effect of χ when rescaling energy only for T=285 K. There it is observed that only a very low χ value is capable of destabilizing the clathrate. Panel b) shows the effect of temperature for a fixed $\chi = 0.035$. There it is seen that the system remains stable for T=250 K and turns clearly unstable for T=300 K. Panel c) shows the effect of varying χ when energy and size is affected for T=285 K. Panel d) shows the effect of temperature at a fixed $\chi = 0.83$. All data confirm the conditions at which the decompositions take place.

Finally, we show the mean-square displacement. This is another property which can be used to notice when the ethane clathrate is being destabilized. Dynamic and structural properties are, of course, linked. When the crystalline compound is simulated in a stable state, the guest molecule has limited displacements due to confinement (we focus attention on the guess molecule only, although similar results are observed for water). Thus as the stable state is being lost because of the temperature increment, the mean-square displacement dramatically increases, denoting the loss of the guest confinement. Figure 9 shows the mean-square displacement over time for SPC water at T=285 K and P=2 MPa. This is shown for three cases. By considering the the energy rescaling of the pair potential with χ=0.035, by considering both, energy and distance rescaling with (χ=0.83), and with no rescaling as a reference. The fluid-like behavior of the mean-square displacement turns obvious for both modified interactions, whereas the reference keeps a solid-like behavior. It is worth mentioning the slightly larger diffusion coefficient (slope of the curve) obtained for the case where the ethane size was decreased. This is a expected result, sites with smaller cross-section areas move faster than those with larger ones.

IV Concluding remarks

Molecular dynamics simulations for ethane clathrates on a NPT ensemble were performed. An exploratory study was carried out over the capabilities of different water models near the region of the phase transition line (pressure – temperature). The estimation of the decomposition temperature was performed by following several structural and dynamical properties. These are the ethane-water coordination number, the total number of hydrogen bonds, the potential energy, and the mean square displacement. All properties are strongly correlated and are appropriate to capture the decomposition of clathrates. The transition stable–unstable crystal compound was observed inside the temperature range of [320–440] K for all considered water models. They all are above the experimental result of 285 K. In this regard, the SPC model produced the closer decomposition temperature whereas the TIP4P/ICE leads to the more stable clathrate (higher decomposition temperature).

In order to approach the experimental decomposition temperature a modification on the cross term of the combining rules was performed by rescaling interaction energy, on the one hand, and interaction energy and distance, on the other. Thus, a scaling factor χ was introduced. We fitted this parameter to reproduce the experimental decomposition temperature. We have obtained $\chi = 0.035$ and $\chi = 0.85$, respectively. Hence, rescaling the intermolecular size is much more effective than rescaling energy alone. This means that the clathrate stability is much more sensitive to the size (hard core) of the guess molecule than to the van der Waals contribution to the energy. In other words, the entropic contribution to the stability seems more important than the enthalpic one.

Acknowledgement

GTG acknowledges CONACyT for supporting his M.Sc studies. DPL thanks to CONACyT for the support through the Cátedra CONACyT program. JLL thanks the financial support from COMECyT (Estancias de investigación científica) and CONACyT, México (Proyect sabbatical/206693). The authors thank the Imperial College High Performance Computing Service for providing computational resource.

References

[1] R.K. McMullan and G.A. Jeffrey, J. Chem. Phys. **42**, 2725 (1965).

[2] T.C.W. Mak and R.K. McMullan, J. Chem. Phys. **42**, 2732 (1965).

[3] J.A. Ripmeester J.S. Tse C.I. Ratcliffe and B.M. Powell, Nature **325**, 135 (1987).

[4] E.D. Sloan, C.A. Koh, Clathrates Hydrates of Natural Gases, (CR Press, Taylor and Francis, Third Edition, 2008)

[5] Y. Jin, M. Kida, and J. Nagao, J. Phys. Chem. C, **117**, 23469 (2013).

[6] K. Shin, K.A. Udachin, I.L. Moudrakovski, D.M. Leek, S. Alavi, C.I. Ratcliffe, and J.A. Ripmeester, PNAS **110**, 8437 (2013).

[7] K.A. Udachin, H. Lu, G.D. Enright, C.I. Ratcliffe, Angew. Chem. Int. Ed. **46**, 8220 (2007).

[8] J. Jhaveri, J. Robinson, Can. J. Chem. Eng. **43**, 75 (1965).

[9] U. Marboeuf, N. Fray, O. Brissaud, B. Schmitt, D. Bockelee-Morvan and D. Gautier, J. Chem. Eng. Data, **57**, 3408 (2012).

[10] R.V. Belosludov, R.K. Zhdanov, O.S. Subbotin, H. Mizuseki, M. Souissi, Y. Kawazoe and V.R. Belosludov, Mol. Sim. **38**, 773 (2012).

[11] K. Tumba, P. Naidoo, A.H. Mohammadi, D. Richon, and D. Ramjugernath, J. Chem. Eng. Data, **58**, 896 (2013).

[12] K. Morita, S. Nakano, K. Ohgaki, Fluid Phase Equlib. **169**, 167 (2000).

[13] H. Erfan-Niya, H. Modarress, E. Zaminpayma, Energy Conversion and Management **52**, 523 (2011).

[14] S.F. Dec, J. Phys. Chem. C **116**, 9660 (2012).

[15] J-W. Lee, S.-P. Kang, Chem. Eng. Trans. **32**, 1921 (2013).

[16] P.R. Bishnoi and V. Natarajan, Fluid Phase Equilib. **117**, 168 (1996).

[17] R.L. Mancera, and A.D. Buckingham, J. Phys. Chem. **99**, 14632 (1995).

[18] D.P. Luis, J. López-Lemus, M. Mayorga and L. Romero-Salazar, Mol. Simul. **36**, 35 (2010).

[19] D.M. Heyes, The Liquid State: Applications of Molecular Simulations, Wiley, Chichester, 1998.

[20] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, and J. Hermans, In Intermolecular Forces, edited by B. Pullman (Reidel, Dordrecht, 1981), p. 331.

[21] H.J.C. Berendsen, J.R. Grigera, and T.P. Straatsma, J. Phys. Chem. **91**, 6269 (1987).

[22] W.L. Jorgensen and J.D. Madura, Mol. Phys. **56**, 1381 (1985).

[23] J.L.F. Abascal and C. Vega, J. Chem. Phys. **123**, 234505 (2005).

[24] J.L.F. Abascal, E. Sanz, R.G. Fernández, and C. Vega, J. Chem. Phys. **122**, 234511 (2005).

[25] J. Alejandre, G.A. Chapela, H. Saint-Martin and N. Mendoza, Phys. Chem. Chem. Phys. **13**, 19728 (2011).

[26] M.W. Mahoney and W.L. Jorgensen, J. Chem. Phys. **112**, 8910 (2000).

[27] S.K. Nath, F.A. Escobedo, and J.J. de Pablo, J. Chem. Phys. **108**, 9905 (1998).

[28] H.A. Lorentz, Ann. Phys. **12**, 127 (1881).

[29] D.C. Berthelot, Sur le Melange des Gaz, Compt. Rend. **126**, 1703 (1898).

[30] J. Vrabec, J. Stoll and H. Hasse, Mol. Simul. **31**, 215 (2005).

[31] A.J. Haslam, A. Galindo, G. Jackson, Fluid Phase Equilib. **266**, 105 (2008).

[32] H. Doherty, A. Galindo, C. Vega, E. Sanz, J. Phys. Chem. B, **111**, 8993 (2007).

[33] M. Lasich, A.H. Mohammadi, K. Bolton, J. Vrabec, D. Ramjugernath, Fluid Phase Equilib. **381**, 108 (2014).

[34] M.M. Conde and C. Vega, J. Chem. Phys. **133**, 064507 (2010).

[35] I.N. Tsimpanogiannis, N.I. Diamantonis, I.G. Economou, N.I. Papadimitriou, A.K. Stubos, Chem. Eng, Research and design **92**, 2992 (2014).

[36] N.I. Papadimitriou, I.N. Tsimpanogiannis, I.G. Economou, A.K. Stubos, Mol. Phys. **112**, 2258 (2014).

[37] B. Hess, C. Kutzner, D. van der Spoel, E. Lindahl, J. Chem. Theory Comput. **4**, 435 (2008).

[38] E. Lindahl, B. Hess, D. van der Spoel, J. Mol. Mod. **7**, 306 (2001).

[39] H.J.C. Berendsen, D. van der Spoel, R. van Drunen, Comp. Phys. Comm. **91**, 43 (1995).

[40] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, J. Hermans, Interaction Models for Water in Relation to Protein Hydration, in Intermolecular Forces, B. Pullman, ed., D. Reidel Publishing Company, Dordrecht, 331–342 (1981).

[41] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, A. DiNola, J.R. Haak, J. Chem. Phys. **81**, 3684 (1984).

[42] G.J. Martyna, M.L. Klein, M.E. Tuckerman, J. Chem. Phys. **97**, 2635 (1992).

[43] U. Essmann, L. Perera, M.L. Berkowitz, T. Darden, H. Lee, L.G.J. Pedersen, J. Chem. Phys. **103**, 8577 (1995)

[44] B. Hess, H. Bekker, H.J.C. Berendsen, J.G.E.M. Fraaije, J. Comput. Chem. **18**, 1463 (1997).

[45] R.K. McMullan and G.A. Jeffrey, J. Chem. Phys. **42**, 2725 (1965).

[46] J.D. Bernal and R.H. Fowler, J. Chem. Phys. **1**, 515 (1933).

[47] D. Chandler, Introduction to Modern Statistical Mechanics, Oxford University Press, New York, 1987.

[48] A. Luzar, D. Chandler, Nature **379**, 55 (1996).

[49] M.P. Allen and D. Tildesley, Computer Simulation of Liquids, Clarendon Press, Oxford, 1987.

[50] A.A. Chialvo, M. Houssa, and P.T. Cummings, J. Phys. Chem. B **106**, 442 (2002).

[51] H. Docherty, A. Galindo, C. Vega, E. Sanz, J. Chem. Phys. **125**, 074510 (2006).

[52] W.L. Jorgensen, D.S. Maxwell and J. Tirado-Rives, J. Am. Chem. Soc. **118**, 11225 (1996).

Figure Caption

Figure 1, CH_3–CH_3 RDF's at T=200 K and P=2 MPa. Different water models were used. Open diamonds TIP5P, crosses TIP4P/ICE, asterisk TIP4P/2005, open triangles TIP4Q, open squares TIP4P, open circles SPC/E and pluses SPC water models.

Figure 2, CH_3–O RDF's at T=200 K and P=2 MPa. Different water models were used. The symbol have the same meaning as figure 1.

Figure 3, Snapshot of the ethane clathrates using SPC water model at T=250 K and P=2 MPa.

Figure 4, coordination number at P=2 MPa as a function of temperature. a) for $\chi = 1$ and b) varying the χ parameter. The symbol have the same meaning as figure 1.

Figure 5, hydrogen-bonds as a function of temperature. Different water models were used. a) for $\chi = 1$ and b) varying the χ parameter. The description for each water model is contained in the inset.

Figure 6, potential energy at P=2 MPa. a) the lower curve corresponds to the results derived at T=285 K, the upper curve was calculated at T=330 K, using standard Lorentz-Berthelot combining rules in both cases. The curves which are between the previous ones were calculated at T=285 K including the χ parameter in the combining rules. The continues line was derived by using the $\chi = 0.83$ and the curve with up-triangles correspond to results from $\chi = 0.035$. b) The OPLS/AA on ethane molecule was used with $\chi = 0.083$, the curves from bottom to top correspond to results derived at T=285K (open squares), T=230K (open diamond) and T=340K (open down-triangles), respectively.

Figure 7, CH_3–CH_3 RDF's as a function of temperature using standard Lorentz-Berthelot rules at P=2 MPa. The description of the curves is contained in the inset.

Figure 8, CH_3–CH_3 RDF's at P=2 MPa using the SPC water model for these simulations. As a first approximation the combining rule for ϵ_{ij} was modified with the χ parameter, a) fitting the temperature and varying the parameter χ. b) fitting the χ parameter and varying the temperature. The second approximation both combining rules were modified, c) for T=285K and varying the χ parameter and d) fitting the $\chi = 0.83$ parameter but varying the temperature. See the inset for the meaning of the symbols.

Figure 9, MSD at T=285 K and P=2 MPa. The open up-triangles correspond to the results estimated with $\chi = 1$. The open circles are the results calculated with $\chi = 0.035$, where just the ϵ_{ij} parameter was modified. The open squares were obtained from $\chi = 0.83$ when the both the arithmetic and geometric combining rules were modified at the same time.

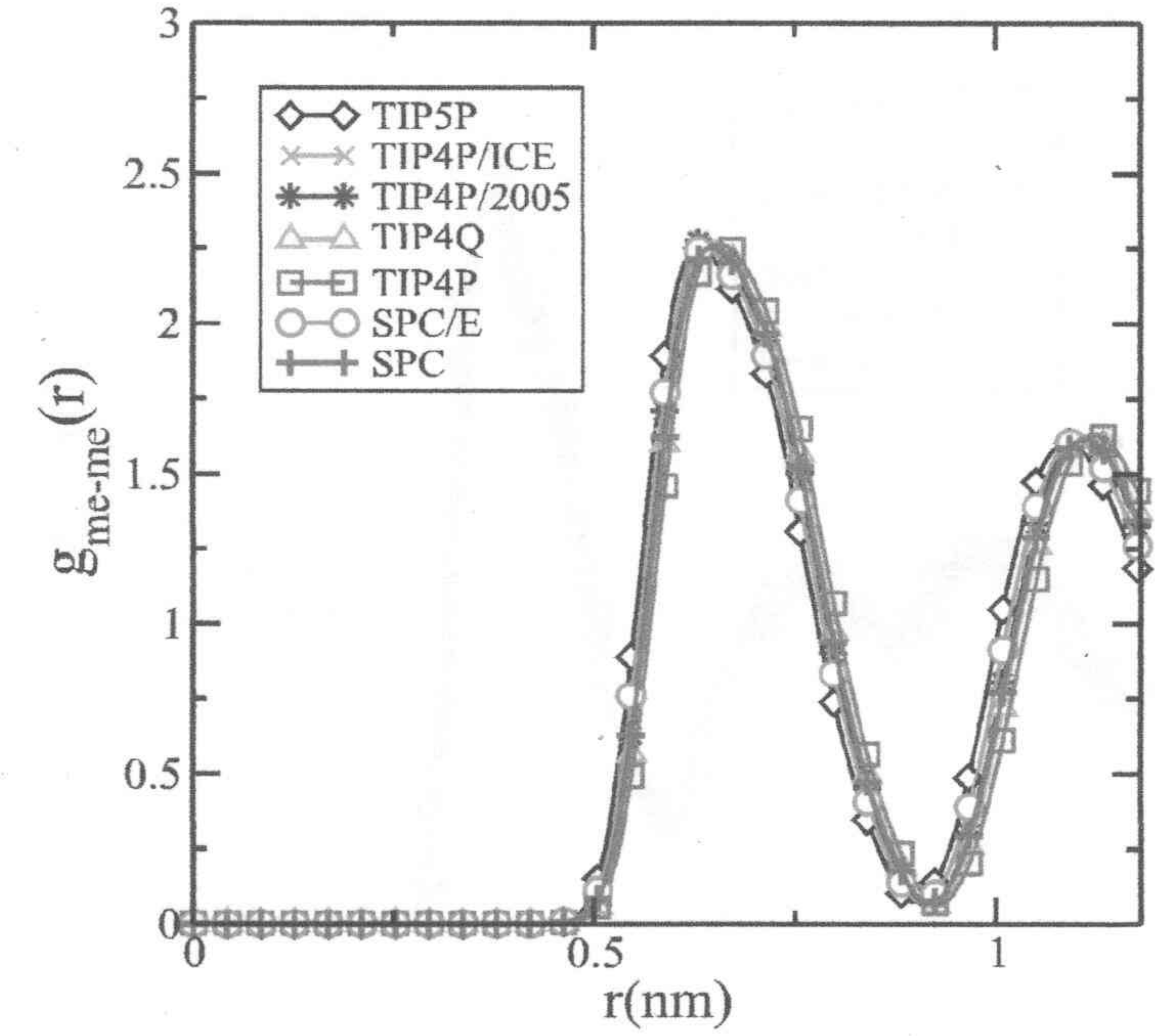


Figure 1, CH_3–CH_3 RDF's at T=200 K and P=2 MPa. Different water models were used. Open diamonds TIP5P, crosses TIP4P/ICE, asterisk TIP4P/2005, open triangles TIP4Q, open squares TIP4P, open circles SPC/E and pluses SPC water models.

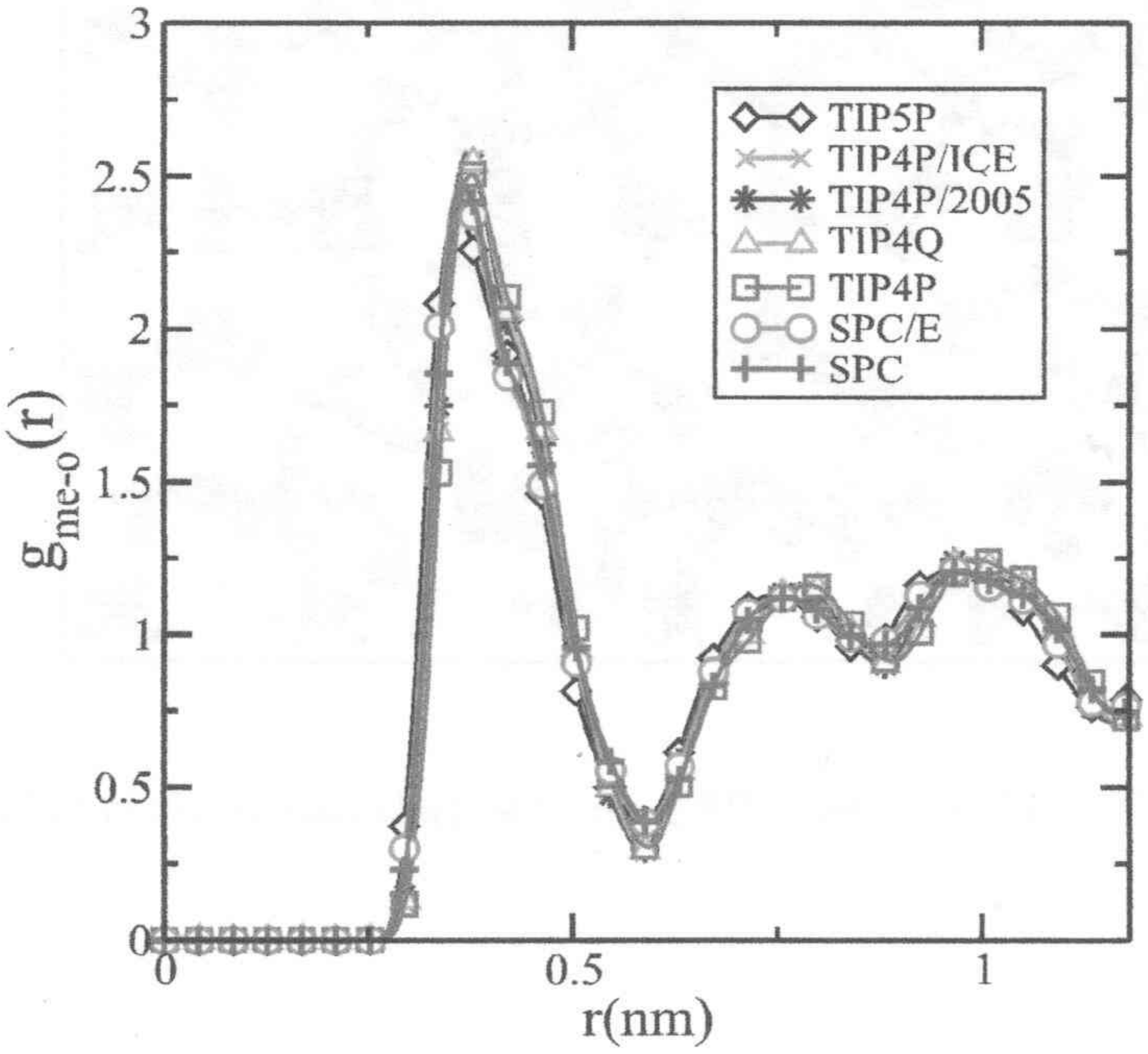


Figure 2, CH_3–O RDF's at T=200 K and P=2 MPa. Different water models were used. The symbol have the same meaning as figure 1.

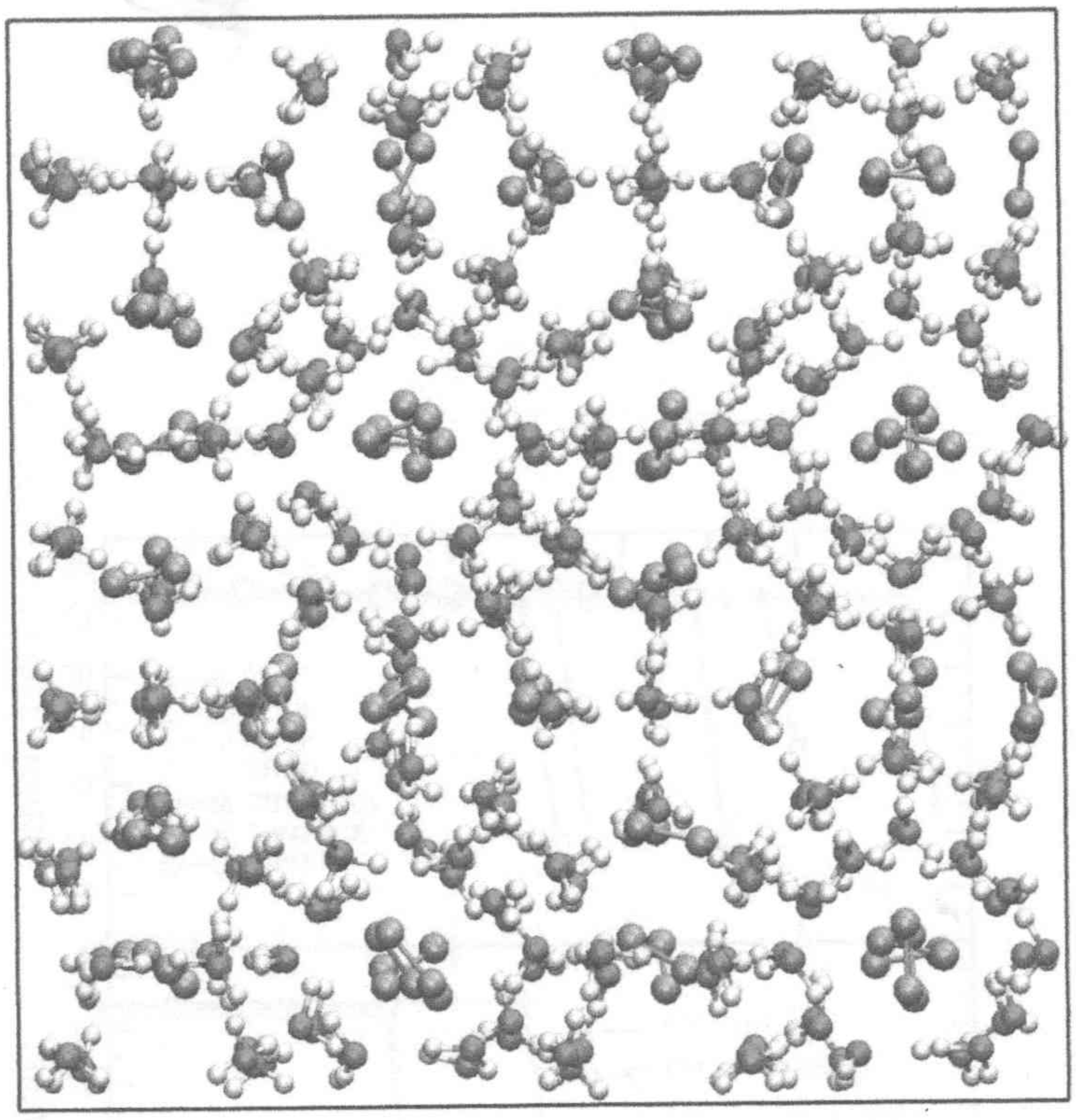


Figure 3, Snapshot of the ethane clathrates using SPC water model at T=250 K and P=2 MPa.

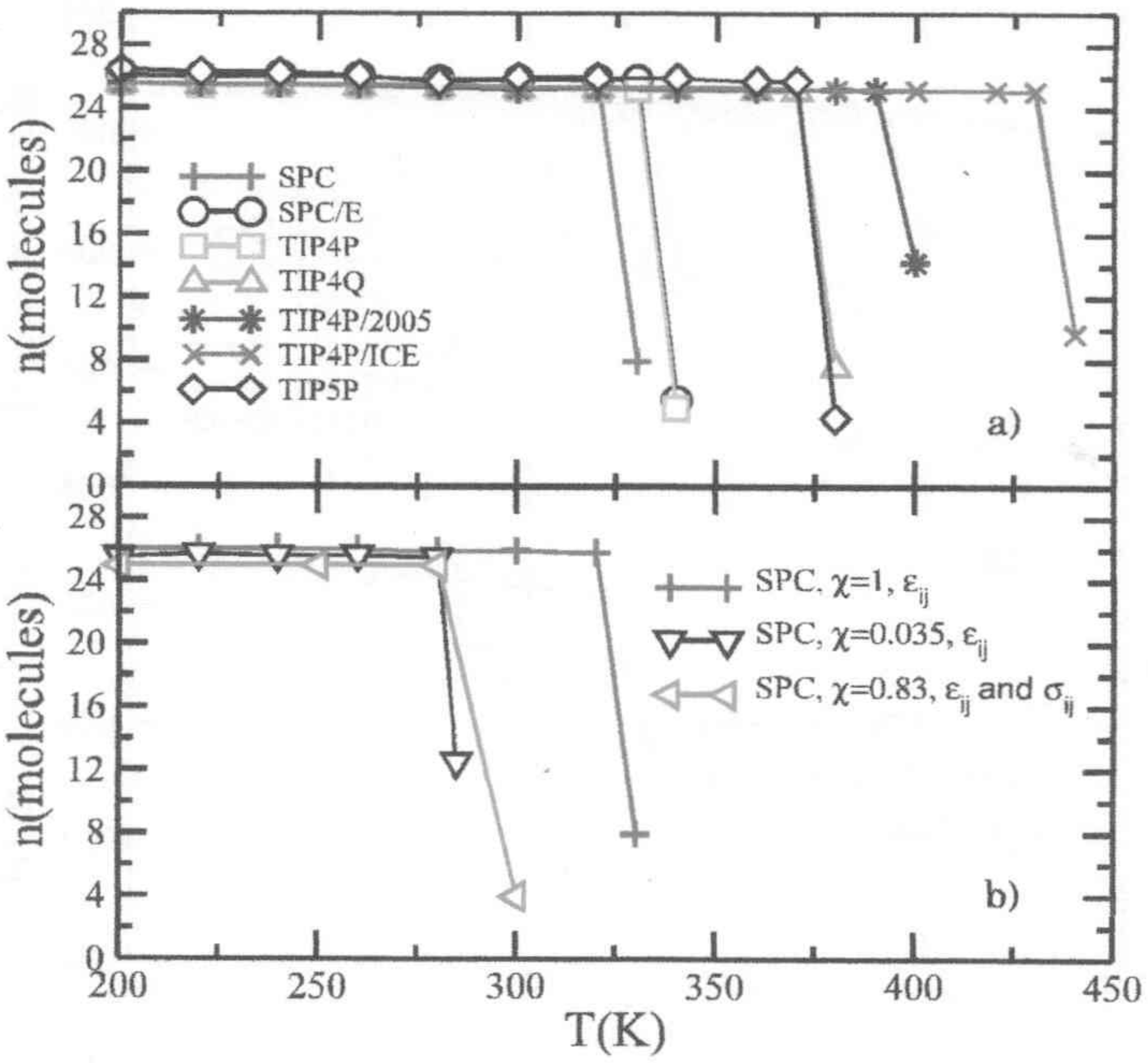


Figure 4, coordination number at P=2 MPa as a function of temperature. a) for $\chi = 1$ and b) varying the χ parameter. The symbol have the same meaning as figure 1.

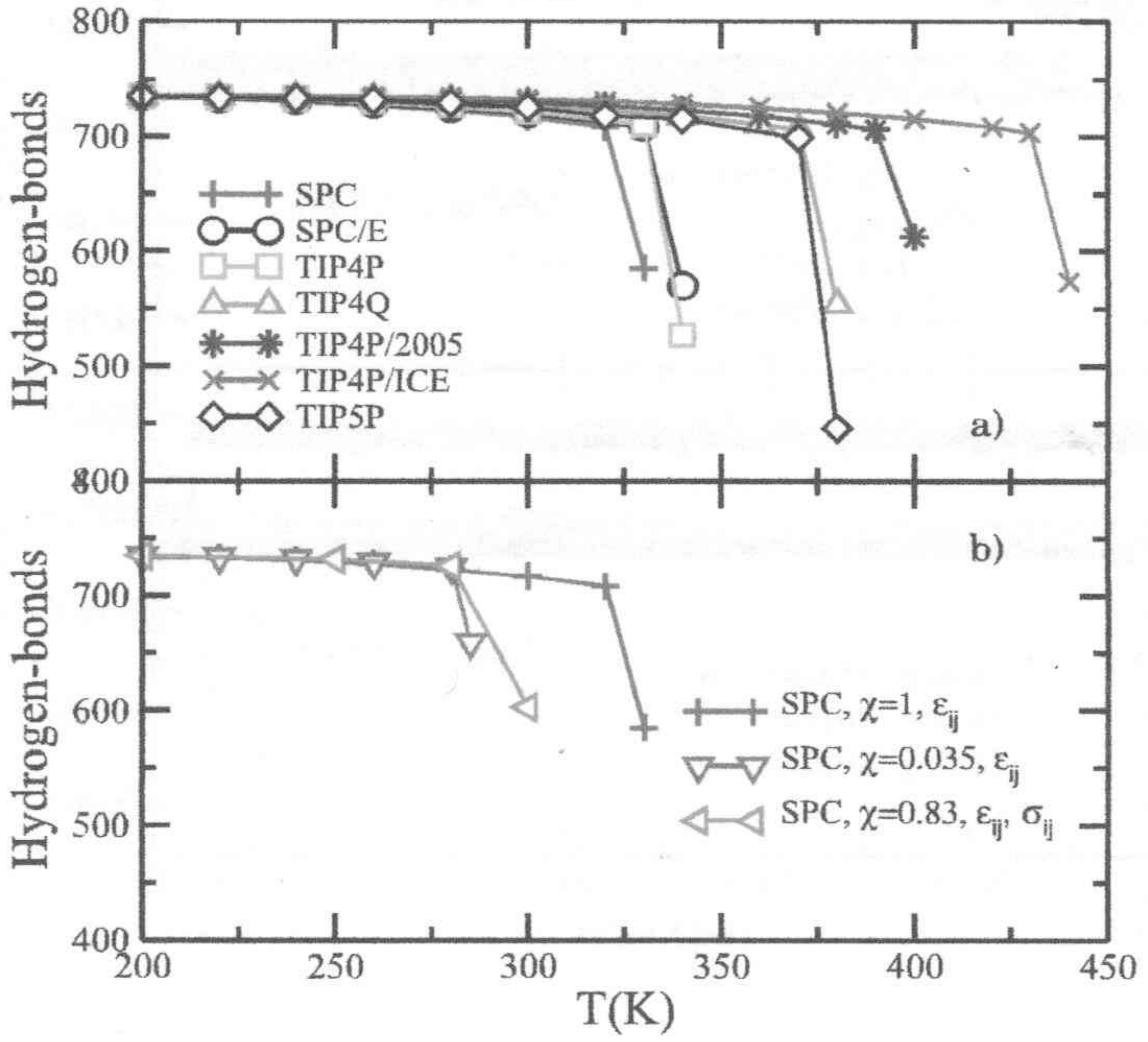


Figure 5, hydrogen-bonds as a function of temperature. Different water models were used. a) for $\chi = 1$ and b) varying the χ parameter. The description for each water model is contained in the inset.

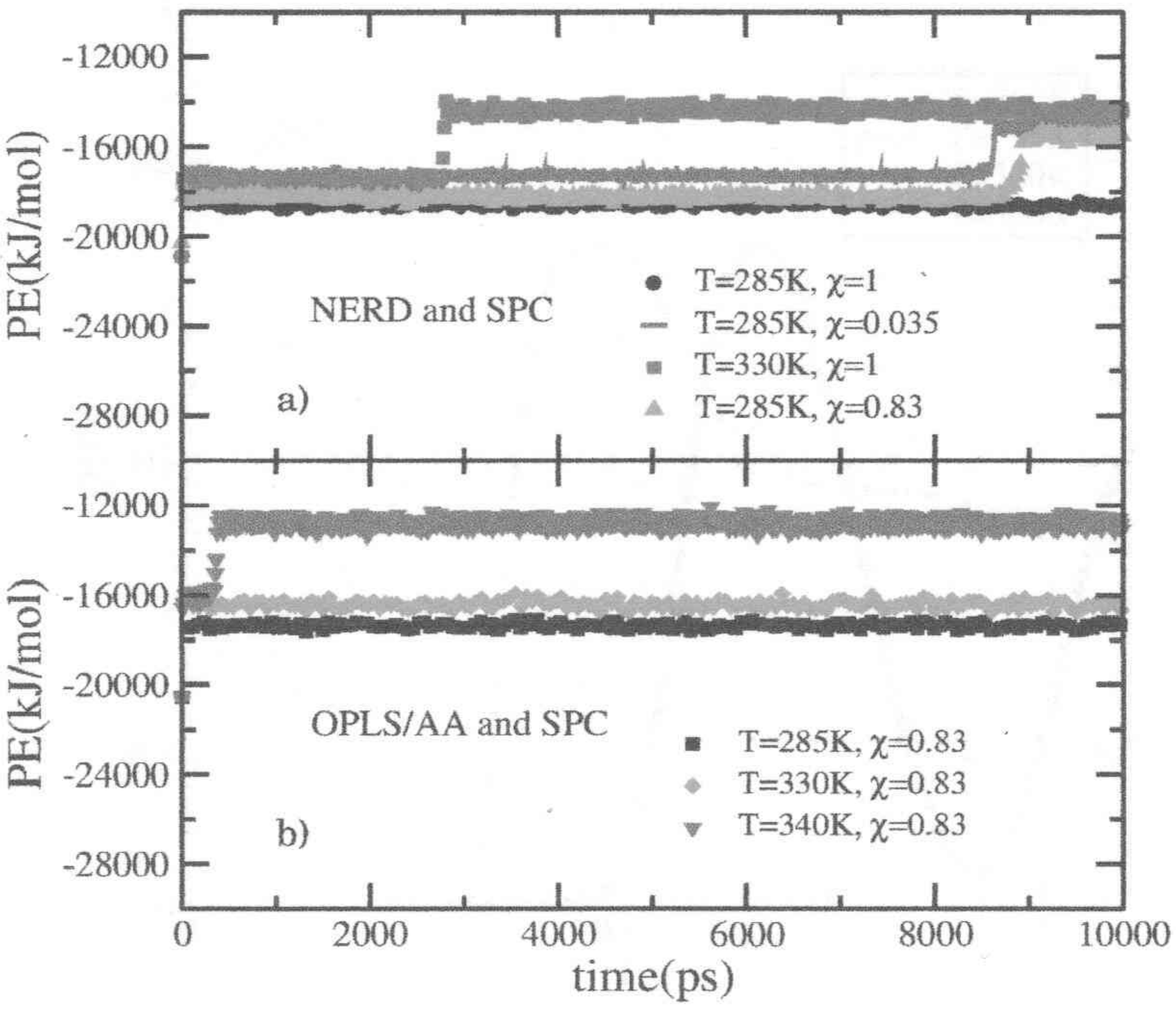


Figure 6, potential energy at P=2 MPa. a) the lower curve corresponds to the results derived at T=285 K, the upper curve was calculated at T=330 K, using standard Lorentz-Berthelot combining rules in both cases. The curves which are between the previous ones were calculated at T=285 K including the χ parameter in the combining rules. The continues line was derived by using the $\chi = 0.83$ and the curve with up-triangles correspond to results from $\chi = 0.035$. b) The OPLS/AA on ethane molecule was used with $\chi = 0.083$, the curves from bottom to top correspond to results derived at T=285K (open squares), T=230K (open diamond) and T=340K (open down-triangles), respectively.

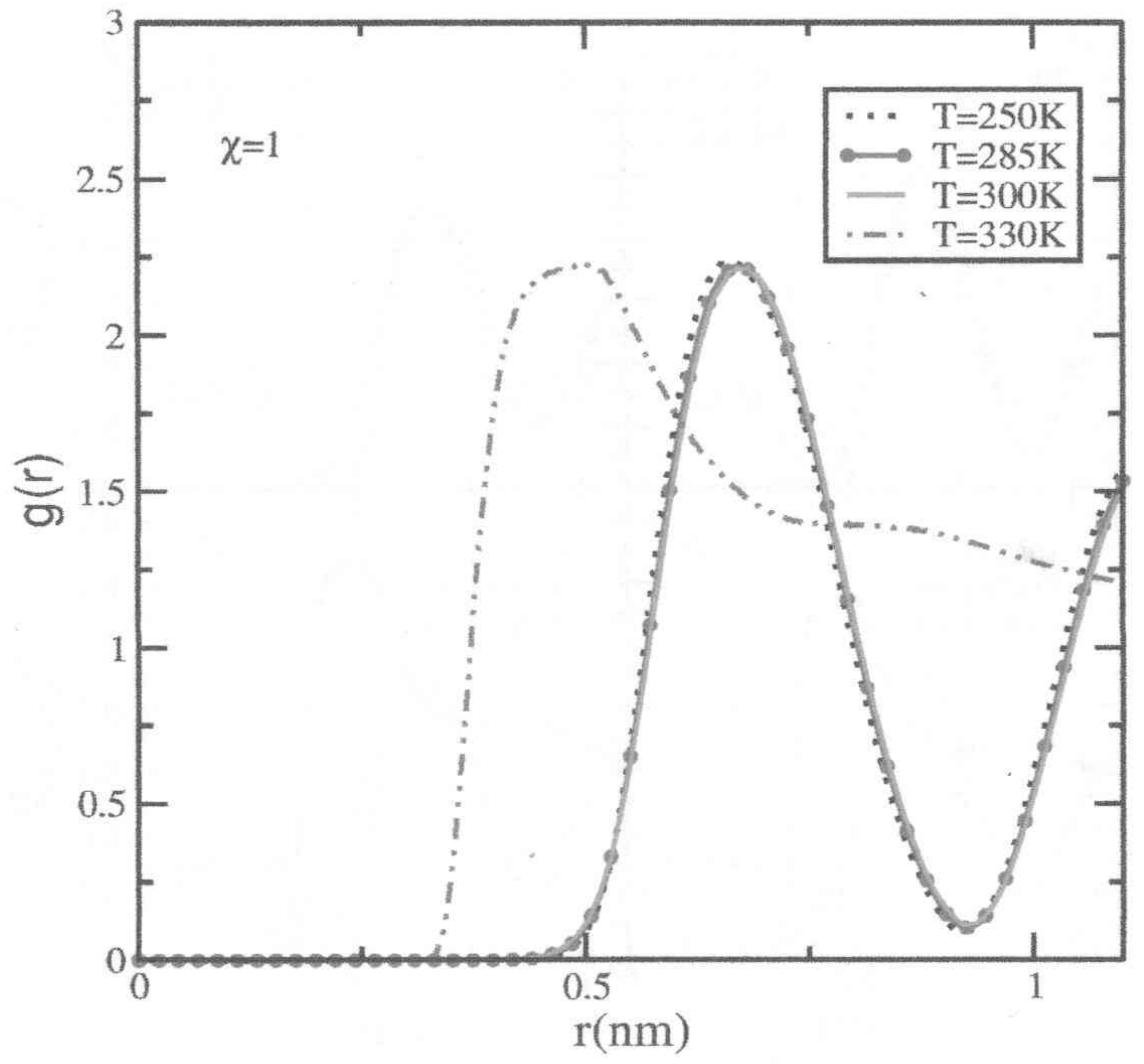


Figure 7, CH_3–CH_3 RDF's as a function of temperature using standard Lorentz-Berthelot rules at P=2 MPa. The description of the curves is contained in the inset.

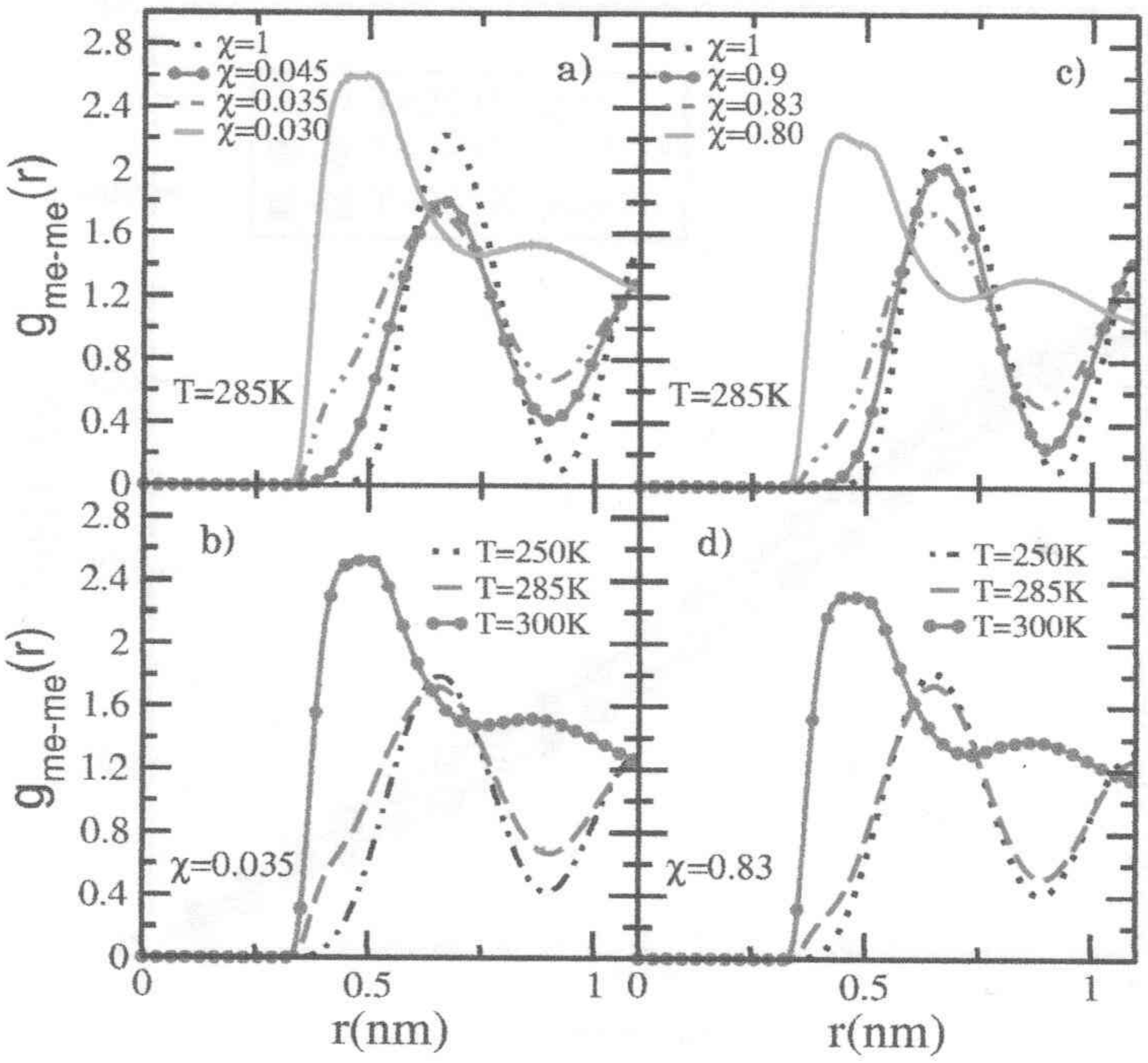


Figure 8, CH_3–CH_3 RDF's at P=2 MPa using the SPC water model for these simulations. As a first approximation the combining rule for ϵ_{ij} was modified with the χ parameter, a) fitting the temperature and varying the parameter χ. b) fitting the χ parameter and varying the temperature. The second approximation both combining rules were modified, c) for T=285K and varying the χ parameter and d) fitting the $\chi = 0.83$ parameter but varying the temperature. See the inset for the meaning of the symbols.

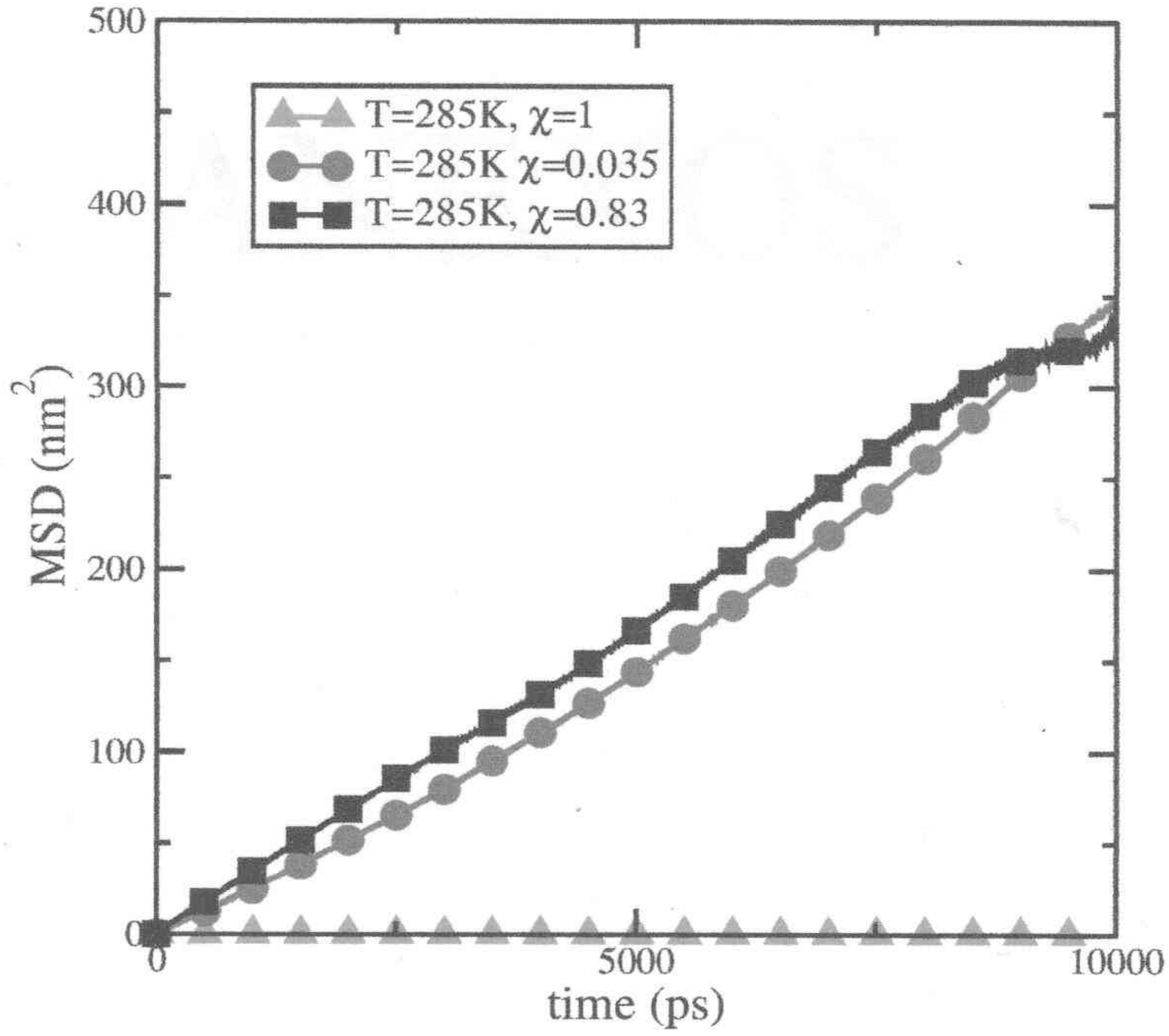


Figure 9, MSD at T=285 K and P=2 MPa. The open up-triangles correspond to the results estimated with $\chi = 1$. The open circles are the results calculated with $\chi = 0.035$, where just the ϵ_{ij} parameter was modified. The open squares were obtained from $\chi = 0.83$ when the both the arithmetic and geometric combining rules were modified at the same time.