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**Microscopic pressure-cooker model for studying molecules in confinement**

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A model for a system of a finite number of molecules in confinement is presented and expressions for determining the temperature, pressure, and volume of the system are derived. The present model is a generalisation of the Zwanzig–Langevin model because it includes pressure effects in the system. It also has general validity, preserves the ergodic hypothesis, and provides a formal framework for previous studies of hydrogen clusters in confinement. The application of the model is illustrated by an investigation of a set of prebiotic compounds exposed to varying pressure and temperature. The simulations performed within the model involve the use of a combination of molecular dynamics and density functional theory methods implemented on a computer system with a mixed CPU–GPU architecture.

Keywords: pressure and temperature effects; molecular dynamics; thermodynamic states; electronic structure; confined molecules

Introduction

The behaviour of particles under the effects of pressure and temperature is of great interest. There are several models which can be applied to study this behaviour [1,2]. The models usually assume periodic boundary conditions to avoid physical limits regarding the system size, and introduce additional degrees of freedom in the system to mimic the role of a thermostat and a barostat. Still, pressure and temperature can be introduced to the system in the simulation by including the interaction with an additional set of particles surrounding the particles of interest. In practice, a system of particles placed under confinement and subject to the effects of temperature requires the presence of confining walls limiting its spatial expansion. The walls need to be in contact with a heat reservoir to maintain a constant temperature. Thus, the container has to be allowed to exchange energy with the reservoir, while keeping the pressure of the system at certain value. At the microscopic level, the surrounding medium and the container in the model need to have atomic structures to allow the atoms of the two systems to interact and exchange energy. For instance, as the energy transfer from the heat-bath particles to the container makes the container atoms to vibrate, this vibrational motion propagates to the confined atoms. Achieving the thermodynamic equilibrium of the system in the container usually takes time. After the system is equilibrated, the confined particles appear under different thermodynamic conditions before the energy transfer took place. The model describing this behaviour resembles heating of a pressure cooker.

The purpose of this work is to build a ‘pressure cooker’ model and to derive appropriate equations describing the motion of molecules in a confined system under pressure and temperature. One of the purposes of constructing such a model is to simulate the behaviour of prebiotic compounds in the Miller–Urey experiment [3]. By assuming that the electrons in the system are described by quantum mechanics and the nuclei by Newtonian theory, a Lagrangian of the Zwanzig–Langevin type is proposed for the motion of the particles forming the system. Then, by following standard rules of analytical mechanics, the Lagrangian equations of motion are obtained. The model provides a formal framework for the previous studies of the hydrogen gas under the effects of pressure and temperature [4–11]. Contrary to other proposed models, the present model includes a representation of the medium surrounding the system of the confined particles by a direct inclusion of such properties as the structure and rigidity of the container, the viscosity of the fluid forming the surrounding medium, etc., described in terms of mechanical and statistical mechanics axioms.

The Lagrangian

The formalism used here starts with an expression for the molecular Lagrangian. Care needs to be exercised in dealing with the fact that the Lagrangian is related to the Hamiltonian through a Legendre transformation. This is important because the Hamiltonian is used to represent the particles of...
the heat reservoir surrounding the system according to the statistical mechanics theory [12]. Furthermore, it needs to be ensured that the ergodic hypothesis is preserved in the model. As the model is to be applied to a system with a finite number of particles, the interactions of the atoms forming the container with the atoms of the confined system need to be included and properly described in the simulation. Taking into account all the interactions raises the computational cost of the simulation. This cost increases as more particles are added to the system. In spite of that, the model is of general validity and it is applicable to any number of particles.

The description of the ‘pressure cooker’ model at the molecular level starts with writing a Lagrangian of the Zwanzig–Langvin type for the system consisting of a heat bath and a container holding some number of particles [13]. The Lagrangian describes all particles of the system and accounts for their individual motions and for all inter-particle interactions:

\[ L(q_{ij}, x_i, s_k) = \sum_i \frac{m_i}{2} \dot{x}_i^2 + \sum_i \sum_j \frac{m_{ij}}{2} \dot{q}_{ij}^2 + \sum_i \frac{m'_i}{2} \dot{s}_i^2 - \sum_{i,j} \left[ \frac{m_{ij} \omega_{ij}^2}{2} q_{ij}^2 - c_{ij} q_{ij} x_i + \frac{c^2_{ij}}{2m_{ij} \omega_{ij}^2} x_i^2 \right] - \sum_j \frac{k_j}{2} (x_j - x_j^0)^2 - U(x_i, s_j). \] (1)

Lagrangian \( L(q_{ij}, x_i, s_k) \) involves three types of particles described by the \( q_{ij}, x_i, \) and \( s_i \) coordinates (in the discussion which follows these particles will be called \( q_{ij} \) particles, \( x_i \) particles, and \( s_i \) particles, respectively). The particles of the first type belong to the heat bath (we also refer to these particles as medium or fluid particles). The particles of the second type belong to the container (or cage), and the particles of the third type belong to the confined system, which is being studied. The first three terms in \( L \) represent the kinetic energies of the three types of particles and the next terms represent the inter-particle interactions. The number of particles of the fluid thermal bath is assumed to be very large and they are assumed to vibrate harmonically. These particles are described by coordinates \( q_{ij} \), where the pair of indices \( ij \) indicates that the \( i \)th particle of the container is involved in the interaction with the \( j \)th particle of the fluid. The mass of the \( ij \)th particle of the fluid is \( m_{ij} \). It should be noted that \( m_{ij} \) is different from \( m_{ji} \), \( m_{ij} \neq m_{ji} \). The fluid particles vibrate with angular frequency \( \omega_{ij} \). The particles of the fluid interact with the particles of the container and the interaction is represented by a bilinear form involving coefficients \( c_{ij} \) and expressed in units of energy per square distance. The position vector \( x_i \) corresponds to the \( i \)th particle of the container. This particle has mass \( m_i \). Additional terms are introduced to the Lagrangian to describe harmonic vibrations of the cage particles around their equilibrium positions, \( x_j^0 \). This part of the Lagrangian will be discussed later. The third type of particles are particles located inside the cage. They are described by position variables \( s_i \). The mass of the \( i \)th particle located inside the cage is \( m'_i \). The interaction between particles described by position vectors \( x_i \) and \( s_i \) is represented by the interaction potential \( U(x_i, s_i) \). This potential is determined using \textit{ab-initio} quantum-mechanical calculations using the time-independent Schrödinger equation:

\[ \hat{H} \psi(x_j, s_k) = E \psi(x_j, s_k); \quad U(x_j(t), s_k(t)) = E|_{x_j(t),s_k(t)}. \] (2)

The Hamiltonian \( \hat{H} \) includes all \( x- \) and \( s- \) type particles with their corresponding interactions. The Born–Oppenheimer approximation is assumed in this case. The nuclei move and interact being surrounded by an electron cloud. The electronic energy, \( E \), has parametric dependence on the instantaneous positions \( \{x_j, s_k\} \) and plays the role of the interaction potential for the nuclei. The particles located inside the cage do not directly interact with the fluid particles; however, their state indirectly depends on the state of the fluid particles through the interaction with the particles of the container. Forces \( F_{x_i} \) and \( F_{s_k} \) acting on the \( x_j \) and \( s_k \) particles are obtained by differentiating the interaction potential:

\[ F_{x_i} = -\frac{\partial U(x_i(t), s_k(t))}{\partial x_j}; \quad F_{s_k} = -\frac{\partial U(x_i(t), s_i(t))}{\partial s_k}. \] (3)

Summarising, the Lagrangian, \( L(q_{ij}, x_i, s_k) \), describes the container, which holds the particles of the studied system, submerged in a heat bath. It represents the ‘pressure-cooker’ model with the walls of the cooker formed by the molecular cage.

**Equations of motion**

The following steps are involved in deriving the equations of motion for the pressure-cooker model, according to the rules of analytical mechanics. The equations of motion for the \( x_i \) particles are obtained by the following differentiation [14]:

\[ \frac{d\pi_i}{dt} = \frac{\partial L}{\partial \dot{x}_i}; \quad \pi_i = \frac{\partial L}{\partial \dot{x}_i}. \] (4)

Similar equations of motion are derived for the \( q_{ij} \) and \( s_i \) particles. By using Lagrangian (1), these equations have
the following form:

\[ m_i \ddot{x}_i = \sum_j \left( c_{ij} q_{ij} - \frac{c_{ij}^2}{m_{ij} \omega_{ij}^2} x_i \right) - k_i (x_i - x_i^0) - \frac{\partial U((x_j, s_j))}{\partial x_i}, \]

\[ m_i \ddot{s}_k = -\frac{\partial U((x, s_j))}{\partial s_k}, \quad m_{ij} \ddot{q}_{ij} + m_{ij} \omega_{ij}^2 q_{ij} = c_{ij} x_i. \quad (5) \]

These are second-order differential equations and their number depends on the number of degrees of freedom in the system. There are three types of equations. The first type includes equations corresponding to the particles of the cage. Every particle of the cage interacts with several particles of the fluid and the particles confined inside the cage. The second type includes equations for the pressurised particles located inside the cage. The trajectory of a confined particle directly depends on the other pressurised particles located and on the particles of the cage. It also indirectly depends on the particles of the fluid. The equations of the third type describe the motion of the fluid particles. For simplicity, we assume that each fluid particle interacts only with a single particle of the cage. The next step involves finding the solution of the equations describing the motion of the \( q_{ij} \) particles and using this solution to solve the equations describing the motion of the \( x_i \) particles. The method of parameters variation is applied in this task and the solution which is obtained has the following form [15]:

\[ q_{ij}(t) - c_{ij} \frac{\omega_{ij}}{m_{ij} \omega_{ij}^2} x_i(t) = q_{ij}(0) - c_{ij} \frac{\omega_{ij}}{m_{ij} \omega_{ij}^2} x_i(0) + \frac{k_i(0)}{m_{ij} \omega_{ij}} \sin(\omega_{ij} t) - \int_0^t \cos[\omega_{ij}(t - t')] \dot{x}_i(t') dt'. \quad (6) \]

The values of the particle positions, \( q_{ij}(t) \) and \( x_i(t) \), at time \( t = 0 \) define the initial conditions for the coordinates and the momenta \( (\dot{k}_{ij} = m_{ij} q_{ij}) \) of the heat-bath particles. Note that the term containing \( \dot{x}_i(t) \) in Equation (1) is transformed into a term proportional to \( \dot{x}_i \) (due to differentiation with respect to time) in the equation of motion (5), and is absorbed into Equation (6) because the fluid particles are coupled to the cage particles. It is due to this term that the interaction of the cage particles with the fluid particles is taken into consideration and produces a viscosity term at the statistical level. Next, using the above expression in the equation for \( x_i(t), (5) \), we have

\[ m_i \ddot{x}_i = \sum_j \left\{ c_{ij} q_{ij}(0) - \frac{c_{ij}^2}{m_{ij} \omega_{ij}^2} x_i(0) \right\} \times \cos(\omega_{ij} t) + \frac{c_{ij} k_i(0)}{m_{ij} \omega_{ij}} \sin(\omega_{ij} t) \]

\[- \sum_j \left\{ \frac{c_{ij}^2}{m_{ij} \omega_{ij}^2} \int_0^t \dot{x}_i(t') \cos[\omega_{ij}(t - t')] dt' \right\} \]

\[- k_i (x_i - x_i^0) - \frac{\partial U((x_j, s_j))}{\partial x_i}. \quad (7) \]

The above expression describes the coupling between the motions of the particles of the container and the particles of the fluid. In this point, we only have to solve two types of equations of motion, i.e. the one given above and the equation of motion for the \( s_j \) particles given by Equation (5). However, the above expression is complicated and requires simplification. This is accomplished by combining the effects due to all heat-bath particles into just two terms. Since we are not interested in describing every particle of the heat reservoir, a collective approach is used to represent the effects of the fluid particles. In this approach, we define the so-called ‘noisy source’, \( G_i \), and the so-called dissipative kernel, \( K_i \), both of statistical nature:

\[ G_i(t) = \sum_j c_{ij} \left\{ \frac{k_i(0)}{m_{ij} \omega_{ij}} \sin(\omega_{ij} t) + \frac{q_{ij}(0)}{m_{ij} \omega_{ij}} x_i(0) \cos(\omega_{ij} t) \right\}, \]

\[ K_i(t - t') = \frac{1}{m_i} \sum_j \frac{c_{ij}^2}{m_{ij} \omega_{ij}^2} \cos[\omega_{ij}(t - t')]. \quad (8) \]

The stochastic force, \( G_i \), introduces: (1) a dependence of the fluid particles and the cage particles on the initial conditions, and (2) a set of frequencies that make \( G_i \) be a so-called ‘coloured noise’ force. The dissipative kernel, \( K_i \), is a function of the coupling coefficients, \( c_{ij} \). It correlates the past time, \( t' \), with the present time, \( t \), by introducing a dependence on the time difference, \( t - t' \). The \( K_i \) function is the kernel of the integral over time (see Equation (7)) and can be considered as a memory function. The equation of motion for the \( x_i \) particles is now written in terms of the kernel, \( K_i \), and the stochastic force, \( G_i \), as

\[ m_i \ddot{x}_i = -k_i (x_i - x_i^0) - \frac{\partial U((x_j, s_j))}{\partial x_i} \]

\[- m_i \int_0^t K_i(t - t') \dot{x}_i(t') dt' + G_i(t). \quad (9) \]
This expression describes the behaviour of the $i$th particle of the cage immersed in the heat bath. The particle interacts with the other cage particles and with the particles located inside the cage. Equation (9) is still difficult to solve and a further simplification needs to be made. The simplification is based on a model describing the response of a capacitor to a set of subsequent electric square pulses. This model is applied to describe a particle with short time intervals of mobility due to thermal fluctuations of the fluid. Accordingly, the memory function is represented as a set of subsequent square pulses appearing at regular time intervals. In this case, the speed is an exponential pulse function due to thermal fluctuations of the fluid. This model is applied to describe a particle with short time intervals of mobility due to thermal fluctuations of the fluid. The speed of the particle $v_i(t)$ is a function of the local friction of the medium and the local friction of the medium.

\[ m_i \frac{d^2x_i(t)}{dt^2} = -k_i \left(x_i(t) - x_0^i\right) - \frac{\partial U(x_i, s_k)}{\partial x_i} + G_i(t) - m_i \xi_i \frac{dx_i(t)}{dt}, \]

\[ m'_k \ddot{s}_k = -\frac{\partial U(x_i, s_j)}{\partial s_k}. \]  

(10)

The first of the above equations is the Langevin equation. The set of particles $x_i$ describes a Brownian body with an atomic structure holding a set of particles inside. The last two terms of the equation have a non-potential origin because they are statistical terms representing the net effect of the fluid particles having on the container. The force term containing $\xi_i$ introduces the local friction of the medium. The force $G_i$ represents random interactions exerted by the medium on the $i$th particle of the container. Such terms favour the exchange of energy with the fluid, but make the equation of motion of particle $x_i$ time irreversible due to the random terms that are unpredictable in nature.

**Integrating the equations of motion**

The two above-described differential equations are coupled and need to be solved in an iterative (self-consistent) manner. When this is done, the coordinates $x_i(t_1), x_i(t_2), \ldots$ provide the trajectory of the $i$th cage particle interacting with all other particles of the system. Similarly, the coordinates $s_k(t_1), s_k(t_2), \ldots$ provide the trajectory of the $k$th particle located inside the cage and interacting with the cage particles and other particles located inside the cage. Integration of the equation for $x_i(t)$ leads to [16–18]:

\[ x_i(t_{n+1}) = x_i(t_n) + c_1 v_i(t_n) \Delta t + c_2 \frac{F_i(t_n)}{m_i} \frac{\delta t^2}{2} + X_n' \frac{\delta t}{2}, \]

\[ v_i(t_{n+1}) = v_i,1/2(t_n) + c_1 c_2 \frac{F_i(t_n)}{m_i} \frac{\delta t}{2} + V_n' \frac{\delta t}{2}, \]

(11)

$F_i$ defines the net force exerted on the $i$th particle belonging to the cage. This force is due to the interaction of the $i$th particle with the other particles of the cage and with the particles located inside the cage. The force is determined following the ab-initio calculation of the potential as: $F_i = -\partial U(x_i, s_k) / \partial x_i$. The terms $X_n$ and $V_n$ are the stochastic position and the stochastic speed of the $i$th particle, respectively. These quantities, obtained by integrating the force $G_i$, depend on the interaction of the particle with the heat bath. The coefficients $c_i$, with $i = 0, 1, 2$, depend on the time step, $\delta t$, and on the friction coefficient of the medium, $\xi_j = \xi_i$. They can be calculated in a recursive manner. For small $x = \xi \Delta t$, we have [17]

\[ c_0 = e^{-x} = 1 - x + \frac{x^2}{2} - \frac{x^3}{6} + \frac{x^4}{24} - \frac{1}{120} x^5 + \cdots \]

\[ c_1 = 1 - c_0 = 1 - \frac{x}{2} + \frac{x^2}{6} - \frac{x^3}{24} + \frac{1}{120} x^4 + \cdots \]

\[ c_2 = 1 - c_1 = 1 - \frac{x}{2} + \frac{x^2}{6} - \frac{1}{24} x^3 - \frac{1}{120} x^4 + \cdots \]  

(12)

Expression (10), which describes the behaviour of the particles located inside the cage, is integrated using the standard velocity-Verlet integrator procedure:

\[ s_k(t_{n+1}) = s_k(t_n) + u_k(t_n) \Delta t - \frac{1}{2m'_k} \frac{\partial U(x_i, s_k)}{\partial s_k} \frac{\delta t^2}{2}, \]

\[ u_k(t_{n+1}) = u_k(t_n) - \frac{1}{2m'_k} \left[ \frac{\partial U(x_i, s_k(t_n))}{\partial s_k} + \frac{\partial U(x_i, s_k(t_{n+1}))}{\partial s_k} \right] \Delta t. \]  

(13)

The speed of the particle $s_k$ is $\dot{s}_k = u_k$. The superscript $s$ is added to distinguish the speed of an $s_k$ particle from the speed of an $x_i$ particle. The interaction potential, $U$, and, henceforth, the force on the particle $s_k$ are computed on the fly in the dynamic simulation. No stochastic terms appear in the last set of equations, as the particles inside the cage have no direct contact with the fluid.

The total energy is computed by adding the kinetic and potential energies of the individual particles. According to the equipartition theorem, the kinetic energy of the particles of the fluid in the thermodynamic equilibrium is proportional to the temperature. Therefore, in the simulation performed at constant temperature, the total kinetic energy of the fluid particles is approximately constant and, in principle, can be removed from the expression for the total energy of the system, as it only shifts the energy value by a constant. Also, as the fluid particles are weakly coupled to the cage particles, the contribution to the total energy from...
The interactions of these two types of particles is neglected. With that the total energy is

\[ E_{\text{tot}} = \sum_i \frac{1}{2} m_i \dot{x}_i^2 + \sum_i \frac{1}{2} m_i \dot{s}_i^2 + \sum_i \frac{k_i}{2} (x_i - x_i^0)^2 + E([x_j, s_k]). \]  

(14)

The kinetic energies of the cage particles and the particles located in the cage are described by the first two terms in the above equation. The following terms correspond to the potential energy contributions. The first of these terms is the harmonic vibrational potential energy and the second one is the ab-initio energy obtained from Equation (2). The total energy is not conserved with time due to the stochastic random terms (which reflect the fluctuation-dissipation nature of the medium [19]) in the equations of motion for the \( x_i \) particles. The approach is valid in a general case and applies equally to small and large systems of particles.

**Distribution function of the cage particles in the fluid**

Expression (10) contains random terms that introduce the fluctuation-dissipation effects of the fluid on the cage particles. These stochastic contributions should be dependent on the distribution function compatible with the macroscopic characteristics of the fluid. Thus, the next task is to determine the distribution function from which the random terms of Equation (10) can be determined. This problem was, in fact, first discussed by Chandrasekhar back in 1945 [20]. The probability distribution function in the phase space, \( W(r, v, t) \), depends on time. The distribution function at time \( t + \delta t \) is deduced from the probability distribution function at an earlier time \( t \) by integration. The time evolution of the system is described as a Markoff process. Thus, we have

\[ W(r, v, t + \delta t) = \int \int W(r - \Delta r, v - \Delta v, t) \times p(r - \Delta r, v - \Delta v; \Delta r, \Delta v) d(\Delta r) d(\Delta v). \]  

(15)

Function \( p \) in the above equation is a transition probability of \( W \) evolving from time \( W(t) \) to \( W(t + \delta t) \). The transition probability is a function of the velocity and, by assuming Dirac delta functions for the positions, the transition probability becomes a product and has the following form:

\[ p(r, v; \delta r, \delta v) = p(r, v; \delta v) \delta(\Delta x - v_1 \Delta t) \times \delta(\Delta y - v_2 \Delta t) \delta(\Delta z - v_3 \Delta t). \]  

(16)

Using this form of \( p \) in Equation (15) leads to integrals over the velocity components:

\[ W(r, v, t + \delta t) = \int \int W(r - v \delta t, v - \delta v, t) \times p(r - v \delta t, v - \delta v; \delta v) d(\delta v). \]

By expanding the functions in power series (this is consistent with the Markoff process), it is possible to transform the integral equation into a boundary-value problem of partial differential equations:

\[ \frac{D}{Dt} W = \xi \div_r(Wv) + \xi \frac{k_B T}{m} \nabla^2 W; \]

\[ \frac{D}{Dt} = \frac{\partial}{\partial t} + v \cdot \nabla_r + F \cdot \nabla_v. \]  

(17)

The solution of this equation, together with the second moments of the position and velocity of a Brownian particle, leads to the following bivariate probability distribution function:

\[ W(X_n(\delta t), V_n(\delta t)) = \frac{1}{2\pi \sqrt{ac - b^2}} \exp\left(\frac{-aX_n^2 - 2bX_nV_n + cV_n^2}{2(ac - b^2)}\right), \]

\[ a = \langle V_n^2(\delta t) \rangle; \]

\[ b = \langle X_n(\delta t) V_n(\delta t) \rangle; \]

\[ c = \langle X_n^2(\delta t) \rangle. \]  

(18)

Constants \( a, b, \) and \( c \) correspond to the second moments of the Brownian particle and are given in terms of the friction constant \( \xi \), temperature \( T \) of the fluid, and mass \( m \) of the Brownian particle. In case \( x = \xi \delta t \ll 1 \), the second moments are expanded in power series:

\[ \langle X_n^2(\delta t) \rangle = \frac{2k_B T}{3m} x \delta t \left[ 1 - \frac{3x^2}{4} + \frac{7x^4}{20} - \frac{31x^6}{840} + \frac{3x^8}{320} + \ldots \right], \]

\[ \langle V_n^2(\delta t) \rangle = \frac{2k_B T}{m} x \left[ 1 - x + \frac{2x^3}{3} - \frac{x^5}{15} + \frac{2x^7}{45} + \ldots \right], \]

\[ \langle X_n(\delta t) V_n(\delta t) \rangle = \frac{k_B T}{m} x \delta t \left[ 1 - x + \frac{7x^2}{12} - \frac{x^4}{4} + \frac{31x^6}{360} - \frac{x^8}{40} + \ldots \right]. \]  

(19)

The distribution function, \( W \), described by Equations (18) and (19) determines the stochastic terms, \( X_n \) and \( V_n \), used in Equations (11) for describing the time evolution of the particles forming the container. The distribution function, \( W \), is not only consistent with the Langevin equation of motion (10), but also it is compatible with both the equipartition theorem, which involves the speed of the particle in the fluid, and with the diffusion equation, which describes the position of this particle as a function of time [20].
Expressions (19) show that the friction is the main mechanism through which the particles dissipate energy into the thermal energy. Conversely, the thermal fluctuations can be transferred to the internal energy of the particles. The two processes complement each other and an equilibrium between them can be established. When the number of particles of the cage is small (compared to the number of particles of the fluid, which is usually the case) and the interaction between the cage and the fluid is sufficiently weak that it can be neglected, the distribution function of the fluid particles is that of the canonical ensemble (this can be shown by relating the Lagrangian (1) with the Hamiltonian of the fluid particles) [21,22]. In short, the distribution function, \( W \), can be used to compute the probabilistic mobility of the particles forming the container.

**Thermodynamic observables: volume, temperature, and pressure**

It is necessary to define such thermodynamic observables as temperature, volume, and pressure to determine the thermodynamic state of the particles confined in the cage (Brownian body). The temperature of the container was discussed previously. It appears in the distribution function and thus its statistical value is determined. This value can be verified by comparison with the value obtained from the mechanical consideration.

The next observable to be determined is the volume. It is determined from the geometrical description of the particles confined in the cage. As the fullerene cage is spherical, the volume of the confined atoms is

\[
V = 4\pi R_{conf}^3 / 3; \quad R_{conf} = R_{part} + [R_{cage} - R_{part}] / 2. \tag{21}
\]

The average radius of the sphere containing the confined particles is \( R_{conf} \) and the radius of the fullerene cage is \( R_{cage} \). The quantity \( R_{part} \) is the radius of the confined atoms considered as point particles. The radius of the confinement, \( R_{conf} \), is \( R_{part} \) plus a correction for the electron clouds surrounding the nuclei of the confined atoms located at the interface of the cage and the confined system.

The last quantity to be determined is the pressure. This quantity is a tensor and it is determined using the mechanical approach. In our case, the fullerene cage has a spherical symmetry and the expression for the pressure is simplified. The kinetic contribution to the pressure, \( P_k \), is due to the motion of the confined particles and is computed as \( P_k V = N k_B T \), where \( N \) is the number of confined atoms, \( T \) the equilibrium temperature, \( V \) the volume of the confinement (discussed above), and \( k_B \) is the Boltzmann constant. The static contribution, \( P_s \), to the pressure is due to the interactions between the confined particles and it is calculated from the changes of the potential energy of the confined particles with respect to the volume:

\[
P_s = -\frac{\partial E_{conf}}{\partial V}; \quad E_{conf} = E_{tot} - E_{cage}. \tag{22}
\]

The energy, \( E_{cage} \), is the energy of the empty cage and \( E_{tot} \) is the energy of the whole system, i.e. the atoms of the cage and the confined atoms. The pressure increases when the radius of the fullerene shrinks.

**Equation of state**

The thermodynamic observables, \( P, V \) and \( T \), are the fundamental quantities which appear in the equation of state of the system. Several calculations are required to formulate the equation of state. They involve the determination of the following quantities: the confinement energy in terms of the volume, \( V \), with maintaining the equilibrium temperature.
fixed, and the time-averaged $\bar{P}$, $\bar{V}$, and $\bar{T}$. The use of these quantities in the equation of state allows to preserve the ergodic hypothesis. Yet, it is possible to generate a fit of the $\bar{E}_{\text{conf}}$ vs. $\bar{V}$ data and to propose an analytical expression of $E_{\text{conf}}$ in terms of $V$ [23,24] such as

$$E_{\text{conf}}(V) = -(9B_0V_0/\eta^2)[1 - \eta(1 - x)]\exp[\eta(1 - x)],$$

$$x = (V/V_0)^{1/3}; \quad \eta = 3(B'_0 - 1)/2. \quad (23)$$

The parameters $B_0$, $B'_0$, and $V_0$ are obtained by fitting the above analytical expression to the numerical data $\bar{E}_{\text{conf}}$ vs. $\bar{V}$. Hence, the quantities $V$ and $E_{\text{conf}}$ in the analytical expression represent the time-averaged volume and time-averaged energy of the confined system, respectively. The parameters $B_0$, $B'_0$, and $V_0$ are interpreted as the isothermal bulk modulus and its first pressure derivative at zero pressure, while $V_0$ is usually considered the zero-pressure volume [23]. The static pressure, $P_s$, is obtained by applying Equation (22):

$$P_s = [3B_0(1 - x)/x^2]\exp[\eta(1 - x)]. \quad (24)$$
By using this procedure, it was possible, for example, to determine the thermodynamic state of a small number of confined particles, like hydrogen clusters, resulting in an excellent agreement with the experimental measurements performed on the macroscopic solid [10]. It is important to mention that the expressions for $\bar{P}$, $\bar{V}$, and $\bar{T}$ are based on the Newtonian and statistical mechanics. This makes the confinement method independent of the number of the confined atoms/molecules. In this respect, the method is of a general applicability. Extending the model and permitting the particles to escape through pores in the fullerene cage would make the model more realistic and versatile in determining the stability of a set of confined particles at different pressures and temperatures.

**Ionising radiation**

One of the key ingredients in the Miller–Urey experiment is the presence of ultraviolet (UV) radiation (see Figure 2). Making the glass flask holding the molecules of the investigated compounds transparent to the UV radiation allows for the radiation to electronically excite the molecules and remove electrons from them, which resulted in breaking of chemical bonds and in chemical transformations of the systems. In the present simulations, the effect of the radiation is considered in an implicit manner by stochastically breaking a pair of bonds located close to each other at some random moments of time. In such an approach, the interaction of the molecules with the UV electromagnetic field does not need to be explicitly included in the Lagrangian (Equation (1)). After the radiation-striking event and an ejection of an electron, the charge and multiplicity of the system change from $(\text{charge} = -1, \text{multiplicity} = 2)$ to $(0,1)$, assuming that only one electron is removed in the process. In the simulation, the system is permitted to recapture the lost electron (after a few time steps of the simulation) from the surrounding environment (see Table 1). The stochastic breaking of bonds in a given region mimics the net effect of the UV radiation. This is done without an explicit consideration of the interaction of a photon with the electrons of the molecule which, if the photon energy is sufficiently high, may cause a bond breakage.

**Ab-initio method**

In order to perform a molecular dynamics simulation, a procedure for determining the time-independent wave equation given by expression (2) needs to be established. For this, we apply the density functional theory (DFT) method, in particular, the generalised gradient version because it is sufficiently accurate for the molecular energy evaluation, yet computationally efficient and simple to apply. We use the functionals of Becke for the exchange energy [26] and Lee–Yang–Parr for the correlation energy [27], as they have shown the correct behaviour and good accuracy in calculations of confined clusters. The calculations are performed using the standard 6-31G Gaussian basis set. The use of this basis keeps the computational cost of the calculation at a modest level. The dispersion forces play a minor role for pressurised molecules and the long-range interactions are insignificant in comparison with the short-range ones.

In the DFT method, an electronic wave function is constructed in the form of a single determinant using the DFT molecular orbitals. These are determined by self-consistently solving the Kohn–Sham one-electron equations with a threshold convergence of about $10^{-6}$ Hartree in the density matrix and the energy. The DFT calculations are performed using either open- or closed-shell method and the spin-restricted approach. To mimic an absorption of a photon by a molecule and an ejection of an electron, the $-1$ charge and the spin multiplicity 2 of the system are changed to zero charge and spin multiplicity 1. The initial charge and multiplicity of $-1$ and 2 are usually recovered after some time steps in the simulation (see Table 1). The software package used in the simulation is written in Fortran language and is implemented on a CPU–GPU computer workstation. The package uses TeraChem [28], written in CUDA language, for computing the DFT electronic energy. In principle, any other electronic-structure program package, such as, for example, NWChem [29] or Gamess [30], can be used for this purpose. The advantage of employing TeraChem is the possibility to use the graphics processing units (GPUs), as this package is implemented on that platform. This greatly accelerates the calculation. In the present calculations, a single Tesla-K20c GPU card is used. In essence, the CUDA external program for calculating the DFT energy, which runs on GPUs, is included as a subroutine in the Fortran code, which runs on the CPU. Such an approach eliminates the need to modify the source code of the external program which does the electronic structure calculation. The software and the script to run it will be described and made available elsewhere.

**Dynamics history**

In this work, we consider a set of 14 H$_2$O, 8 NH$_3$, and 8 CH$_4$ molecules (114 atoms in total) confined in a cage of a spherical fullerene formed by 180 helium atoms (see Figure 1). This system models the experimental set-up used in the Miller–Urey experiment, where a mixture of H$_2$O, NH$_3$, and CH$_4$ was confined to a glass flask and the chemistry occurring between these systems was studied under the effects of the temperature and pressure. The reason for using inert He atoms to form the fullerene cage is to minimise the chemical interaction between the container and the molecules confined in the cage. Also, using helium minimises the number of electrons associated with the container, what speeds up the calculation. In the Miller–Urey experiment, the cooling of the compounds located inside the flask was done with the...
help of an externally attached coil filled with cold water (a condensation column). In the case of the computer model, as the electrons of the He atoms are strongly localised, the energy transfer through the walls of the cage and the cooling of the molecules located inside the cage are expected to be slow. However, as the simulation involves the distribution function (18), the cooling can be accelerated by applying this function to the atoms located close to the surface of the fullerene cage (the threshold distance to determine which atoms this applies to is 4.0 Å).

In Table 1, we describe the main events of the dynamics simulation. These include the interaction of the confined molecules with the radiation, the time and the rate of shrinking the container, the equilibrium temperature in different time intervals, the periods of the cage cooling, etc. In particular, the temperatures imposed on the...
Table 1. Main events in the dynamics of the container and confined atoms.∗

<table>
<thead>
<tr>
<th>Step</th>
<th>Events</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Set initial conditions</td>
</tr>
<tr>
<td></td>
<td>Number of confined atoms 114</td>
</tr>
<tr>
<td></td>
<td>Number of container atoms 180</td>
</tr>
<tr>
<td></td>
<td>Method RO-BLYP/6-31g</td>
</tr>
<tr>
<td>1–5009</td>
<td>Time step (fs) 1.0</td>
</tr>
<tr>
<td></td>
<td>Equilibrium temperature (K) 400</td>
</tr>
<tr>
<td></td>
<td>Spring constant (Hartree/Å²) 0.459</td>
</tr>
<tr>
<td></td>
<td>Friction constant (ps⁻¹) 5.0</td>
</tr>
<tr>
<td></td>
<td>Charge, multiplicity −1, 2</td>
</tr>
<tr>
<td>5010–8469</td>
<td>Cage shrinking</td>
</tr>
<tr>
<td></td>
<td>Shrinking factor 0.95</td>
</tr>
<tr>
<td></td>
<td>Reference radius (Å) 10.0</td>
</tr>
<tr>
<td></td>
<td>New reference radius (Å) 9.50</td>
</tr>
<tr>
<td>8470–8479</td>
<td>Striking radiation</td>
</tr>
<tr>
<td></td>
<td>Charge, multiplicity 0, 1</td>
</tr>
<tr>
<td></td>
<td>Broken bonds OH, NH</td>
</tr>
<tr>
<td></td>
<td>Ionisation energy (eV) 3.6154</td>
</tr>
<tr>
<td>8480–9009</td>
<td>Electron uptake</td>
</tr>
<tr>
<td></td>
<td>Charge, multiplicity −1, 2</td>
</tr>
<tr>
<td></td>
<td>Energy change (eV) −0.1536</td>
</tr>
<tr>
<td>9010–9199</td>
<td>Cage shrinking</td>
</tr>
<tr>
<td></td>
<td>Shrinking factor 0.95</td>
</tr>
<tr>
<td></td>
<td>Reference radius (Å) 9.50</td>
</tr>
<tr>
<td></td>
<td>New reference radius (Å) 9.02</td>
</tr>
<tr>
<td>9200</td>
<td>Striking radiation</td>
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<tr>
<td></td>
<td>Charge, multiplicity 0, 1</td>
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<tr>
<td></td>
<td>Broken bonds CH, OH</td>
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<td></td>
<td>Ionisation energy (eV) 3.0470</td>
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<tr>
<td>9201–10572</td>
<td>Cooling container atoms</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>Charge, multiplicity −1, 2</td>
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<tr>
<td></td>
<td>Friction constant (ps⁻¹) 7.0</td>
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<td>10573–10583</td>
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</tr>
<tr>
<td></td>
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<td></td>
<td>Broken bonds CH, OH</td>
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<td></td>
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<td>10584–11783</td>
<td>Electron uptake</td>
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</tr>
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<td></td>
<td>Energy change (eV) 0.2677</td>
</tr>
<tr>
<td>11784–11793</td>
<td>Striking radiation</td>
</tr>
<tr>
<td></td>
<td>Charge, multiplicity 0, 1</td>
</tr>
<tr>
<td></td>
<td>Broken bonds OH, OH</td>
</tr>
<tr>
<td></td>
<td>Ionisation energy (eV) 4.7307</td>
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<tr>
<td>11794–11900</td>
<td>Electron uptake</td>
</tr>
<tr>
<td></td>
<td>Charge, multiplicity −1, 2</td>
</tr>
<tr>
<td></td>
<td>Energy change (eV) 0.6022</td>
</tr>
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<td>11901–13000</td>
<td>Cooling container and confined atoms</td>
</tr>
<tr>
<td></td>
<td>Threshold distance to the cage (Å) 4.0</td>
</tr>
<tr>
<td>13001–16000</td>
<td>Cooling container and confined atoms</td>
</tr>
<tr>
<td></td>
<td>Equilibrium temperature (K) 200</td>
</tr>
</tbody>
</table>

∗The events are correlated with the curves of Figure 3.

particles forming the container are 400, 300, and 200 K, with friction constants of 5 and 7 ps⁻¹, and constant spring factor of 0.459 Hartree/ Å². The initial and final values of the temperature and the friction constant are used to determine when to start the heating and cooling processes at the different stages of the simulation. The events described in Table 1 correlate with the curves shown in Figure 3(a), where the temperatures of the cage atoms and the confined molecules are given in terms of time. Figure 3(b) shows the time dependency of the energy, \( E_{\text{conf}} \) (Equation (22)), of
Figure 3. Inset A in the figure shows the temperature variation of the cage atoms and the confined atoms with time. The relevant events of the dynamics, like cooling of the cage atoms, and the effect of incident radiation on the confined atoms are indicated with symbols and colours. The equilibrium temperatures of the cage atoms are also given. The events are correlated with those of Table 1. Inset B in the figure shows the variation of the energy of the confined atoms with time. The units of time, temperature, and energy are fs, K, and Hartree, respectively.

<table>
<thead>
<tr>
<th>Interval</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1000–4500]</td>
<td>400 K</td>
</tr>
<tr>
<td>[5500–9000]</td>
<td>300 K</td>
</tr>
<tr>
<td>[13500–16000]</td>
<td>200 K</td>
</tr>
</tbody>
</table>

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The confined molecules. Both figures show sharp changes at the moments when the radiation strikes the system. One can also see sharp temperature changes with the shrinking and cooling of the cage. The intervals of time where thermal equilibrium of the container occurs are [1000–4500] and [5500–9000] with $T = 400$ K, [9500–13000] with $T = 300$ K, and [13500–16000] with $T = 200$ K. The temperature of the molecules confined inside the cage exhibits
more radical changes, specially in the intervals of the radiation striking. After the shrinking and cooling stages of the container, the temperature of the confined molecules slowly changes. In effect, the thermal equilibrium is achieved at a faster pace. It is only during the final cage cooling that the confined molecules and the cage atoms fully equilibrate and reach the same temperature.

According to the second law of thermodynamics, \[ \Delta Q = \Delta U \] at a constant volume. This means that the energy of the confined molecules depicted in Figure 3(b) increases as more energy transfers to them from the cage atoms. An increase of the cage volume should reduce both the energy and temperature. However, as in the simulation, the temperature is lowered by cooling the fluid (this is done by lowering the temperature in the distribution function), the cooling is transferred to the container (due to fluctuation-dissipation effects) and eventually to the molecules confined in the cage.

The simulations show that, in the case of the prebiotic compounds, the breaking of bonds due to the temperature effects is, as expected, very sporadic. Also, the broken bonds are immediately restored particularly when high pressure is applied. The simulations show the formation of hydrogen-bonded networks of water and ammonia molecules, while the methane molecules show hydrophobic character as they do not participate in the networks. In effect, they are removed from the central region of the container and stay for most of the time close to the container walls. The simulations reveal that the ionising radiation is the main cause of the bond breaking by far exceeding the bond breaking resulting from the temperature effect at the confined conditions studied in this work. In conclusion, it is only due to the radiation that the formation of new compounds is possible. However, some preliminary results concerning simulation of a confined system, where SH2 molecules are introduced to the prebiotic soup, lead to somewhat different results. Future work will need to involve changing the densities or the numbers of the confined molecules and their chemical composition. Addition of light metals as elements of the confined molecules will also be considered. The use of other simulation approaches such as the quantum-mechanics/molecular-mechanics (QM/MM) scheme will also be considered. They may allow to reduce the number of electrons involved in the container by simultaneously increasing the number of confined atoms. Finally, the work presented here is expected to be of help for the development of new force fields that take the effects of temperature and pressure into account. Efforts in this direction have already started by other researchers [31–33].

Acknowledgements

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References

[25] Figure modified after https://cdn-assets.answersingenesis.org/img/articles/ee/v2/miller-urey-experiment.jpg.