# Relaxation Processes in a Dimethylimidazolium Chloride-methanol System

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The molecular dynamics method was used to study the short time relaxation processes in the dimethylimidazolium chloride-methanol system at $T = 400$ K. We demonstrate that the establishment of thermodynamic equilibrium in the $dmim^+/Cl^-$-methanol system is associated with both short-time relaxation processes (β-relaxation) and at relatively long-time relaxation processes. The processes of β-relaxation at $t < 5$ ps are accompanied by the change in the local structure of the $dmim^+/Cl^-$-methanol system. The relaxation time is ~ 3.6 ps, which is the same as the time it takes the methanol molecule to jump by an inter-particle distance. At $t \geq 35$ ps, dynamic processes can be considered within the framework of a relaxation model which describes the structural and dynamic processes in the liquid at relatively large time intervals.

## INTRODUCTION

Thermodynamic equilibrium in ionic liquids, as in any other liquid systems, is attained *via* the shorter (β-relaxation) and longer (α-relaxation) time relaxation processes [1-6]. The α-relaxation is a cooperative phenomenon associated with an increase in length scales, while β-relaxation is determined by local spatial processes, including the motion of a particle in a "transition cell" formed by its neighbors [7-12]. Molecular dynamics approaches in the study of model highly viscous fluid systems demonstrate that β-relaxation has a cooperative nature [13,14]. The time scales used to analyze systems with finite sizes in the case of β-relaxation turn out to be the same as the time and length scales that describe the spatial heterogeneity (heterogeneity of the system) of local dynamics in the long-term mode of α-relaxation. The results obtained by Hurley *et al.* [15] indicate a clear correlation between short-term dynamics and relatively large time structural relaxation in liquid systems. It has been established [16-18] that there are at least two different length scales in liquid systems: a dynamic length scale

associated with the heterogeneity of local dynamics, and a static length scale associated with the existence of short-range ordering in a liquid [13,18]. However, it is not yet clear how the dynamic progresses from short-term to long-term. Theoretical and experimental approaches discussing a close correlation between the long- and short-time dynamic processes have attracted significant attention [19-21].

The study of relaxation processes in ionic liquids (IL) is associated with serious challenges due to the ionic nature of ILs [22-25], making the analysis of thermodynamic characteristics, dissolution processes, and their kinetics difficult. The existing methods developed for the study of molecular liquids do not allow correct analysis of the relaxation processes in IL-based systems. As IL systems can remain in a stable liquid state at sufficiently high temperatures and pressures, the study of relaxation processes (closely related to the establishment of thermodynamic equilibrium), and their diffusion mechanisms requires new approaches for interpreting the experimental results. In this paper, we study the relaxation processes in ionic liquids using the molecular dynamics method. We analyze the changes in the structural-dynamic properties of liquid systems in the time interval of

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up to ~ 150 ps. A classical approach to probing the dynamic processes in liquid focuses on the motion and interaction mechanisms in IL solutions at infinite dilution. In this approach, the interaction of solute molecules with each other is excluded from the analysis.

The aim of this research is to study the relaxation processes in the ionic liquid 1,3-dimethylimidazolium chloride (dmim$^+$/Cl$^-$), -a dissolved substance at a temperature of $T = 400$ K in the time interval up to ~ 150 ps. Methyl alcohol (CH$_3$OH), used as a solute, creates a simple and informative model system for studying the influence of a polar solute on the dynamics of components that are closely related to relaxation processes.

## COMPUTER-BASED EXPERIMENTS

To conduct a computer-based experiment we used the molecular dynamics method in the modified DL_POLY_4.05 software package [26] with a time step of 2 fs. In the calculations, cations and anions of dmim$^+$/Cl$^-$, and methanol were represented as the rigid charged models with a fixed geometry. The geometric parameters of the molecules and the parameters of intermolecular interactions of methanol are shown in Table 1 [27]. The methanol molecule is described in the framework of a triatomic model, in which the alkyl group is represented as a single "effective" atom. Atomic charges of the alcohol molecule are described as follows: it is assumed that the atom of positive charge $q_H$ is located in the hydrogen atom of the hydroxyl group and in an "effective" atom whose role is played by a methyl group. The oxygen atom carries a negative charge $q_O$. Electrical neutrality is then achieved by placing the corresponding charge on the "effective" atom. The parameters of the intermolecular interactions and atomic charges for dmim$^+$/Cl$^-$ [28] are summarized in Table 1; the molecule is shown in Fig. 1.

All calculations were carried out for a system containing 192 dmim$^+$ cations, 192 chlorine anions Cl$^-$, and one molecule of a dissolved substance (methanol) at $T = 400$ K.

To describe interactions between ions at short distances in an ionic liquid, the Buckingham potential is used [29]. The effective intermolecular interaction potential, which can be represented as the sum of the Lennard-Jones and

Coulomb components, was used both to describe the interactions between the components of the ionic liquid at large distances, and to describe the interactions between the components of the IL and the dissolved substance [30]:

$$U = U_{L-D} + U_{Coulomb} = \sum_{ij} 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_{ij} \frac{q_i q_j}{r_{ij}} \quad (1)$$

The values of parameters $\sigma_{ij}$, $\varepsilon_{ij}$, and $q_i$ can be obtained both on the basis of model representations of the interaction, and the analysis of the corresponding experimental data. The values of the potential parameters (1) $\sigma_{ij}$ and $\varepsilon_{ij}$, which describe the interactions of the ionic liquid components with the dissolved substance, were calculated using the Lorentz-Bartlo combination rule. The Berenzen thermostat, outlined in [31], was used to stabilize the system in the NVT ensemble. In the calculations, the electrostatic interaction at short distances was modeled by placing point charges on each atom, and long-range electrostatic interaction was modeled using summation by the Ewald method [32]. To determine the energy characteristics, several series of independent calculations were carried out with steps of 200 fs, 160 fs and 80 fs. Calculations were performed as follows: the investigated system was stabilized in $8 \times 10^5$ steps, followed by another $15 \times 10^5$ steps of calculation. All radial distribution functions (RDFs) were obtained with a step of ~200 fs.

## DISCUSSION

The diffusion of equilibrium liquids in the case of uniform probability dynamics is described by the equation [33]:

$$D\nabla^2 P(r,t) = \frac{\partial P(r,t)}{\partial t} \quad (2)$$

whose solution in spherical coordinates is given by:

$$P_0(r,t) = 4\pi r^2 \left( \frac{3}{2\pi \langle r^2(t) \rangle} \right) \exp\left( -\frac{3r^2}{2\pi \langle r^2(t) \rangle} \right) \quad (3)$$

where $D$ is the diffusion coefficient, and $\langle r^2 \rangle$ is the second spatial moment of the function $P(r,t)$ which determines the

**Table 1.** Charges, $q_i$, Lennard-Jones Parameters, $\sigma_{ij}$ and $\varepsilon_{ij}$, for Methanol [24],
and Dmim$^+$/Cl$^-$ [25]

| Molecule | Atom | $q_i$ | $\sigma_{ij}$ | $\varepsilon_{ij}$ |
|---|---|---|---|---|
| | | (e) | (Å) | (kcal mol$^{-1}$) |
| | H | 0.4350 | 0 | 0 |
| CH$_3$OH | O | -0.7000 | 3.071 | 0.7116 |
| | CH$_3$ | 0.2650 | 3.775 | 0.8665 |
| | N | -0.267 | 3.2500 | 0.71128 |
| | C1 | 0.407 | 3.39967 | 0.35982 |
| | C2 | 0.105 | 3.39967 | 0.35982 |
| C$_5$H$_9$N$_2^+$ | C4 | 0.316 | 3.77500 | 0.86650 |
| | H1 | 0.097 | 2.42146 | 0.06276 |
| | H2 | 0.094 | 2.42146 | 0.06276 |
| Cl$^-$ | Cl | -1.0000 | 4.40100 | 0.41843 |
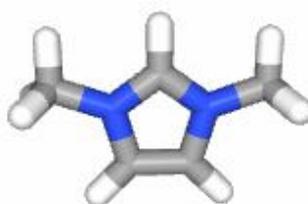


**Fig. 1.** Dimethylimidazolium molecule (dmim$^+$).

mean square particle displacement (MSD). Generally, $<r^2>$ is a function of time.

A linear time dependence $<r^2>$ at the short time intervals indicates Brownian particle dynamics. In this case, diffusion can be calculated as [34]:

$$\langle r^2 \rangle = 6Dt \tag{4}$$

Particle dynamics, characterized by probability density, is homogeneous. Dynamic heterogeneity is manifested in the mean squared displacement of the observed behavior

from the behavior described by Eq. (2). Such mean squared displacement is conveniently described using the non-Gaussian parameter $\alpha(t)$ introduced in [35]:

$$a(t) = \frac{3\langle r^4 \rangle}{5\langle r^2 \rangle} - 1 \tag{5}$$

In the case of homogeneous dynamics, $\alpha(t)$ is equal to zero, and when dynamic heterogeneity occurs, it increases. Non-Gaussian effects are known to be indicative of relaxation processes occurring in the studied liquid system

at different rates [36].

The linear time dependence of the $<r^2>$ functions for all components of the system at $t < 5$ ps indicates the existence of a Brownian-type diffusion due to direct ballistic collisions, and the processes of equilibrium establishment in the system at these times can be described in terms of the β-relaxation model, which includes the short-time diffusion of IL components and restructuring the local structure of the liquid. The analysis presented in Fig. 2 indicates that at $t \sim 5$ ps the mechanism of diffusion changes, and at $t > 5$ ps, diffusion can be described as a slowed average Brownian motion of particles.

Therefore, at $t < 5$ ps, small changes in the mean-square displacement dominate in the dynamic properties of the system, and the motion of particles participating in ballistic collisions at $t > 5$ ps reduces. Moreover, the values of $<r^2>$ of methanol always exceed the corresponding values of $<r^2>$ of the dmim$^+$/Cl$^-$ components. The obtained data are in agreement with the conclusions of Ref. [37], according to which, IL dmim$^+$/Cl$^-$ can be considered as a mixture of large (dmim$^+$) and small particles (Cl$^-$) with a mass ratio $M_{alrge}/M_{small} = M_{dmim} / M_{Cl} = 2.7$ , and structural rearrangement in dmim$^+$/Cl$^-$ is determined by relaxation processes.

Considering the fact that the linear time dependence for short times indicates Brownian dynamics [38], we can assume that the motion of the dmim$^+$/Cl$^-$ components is Brownian, and their diffusion can be calculated using expression (4). At $t > 10$ ps, a plateau is observed in the time dependence of the mean-square displacement of chlorine anions and methanol molecules, which can be caused by the formation of a chlorine anions-methanol system due to the strong Coulomb interaction and the existence of clusters from components of the ionic liquid, which in turn, results in a violation of the system homogeneity. This conclusion is confirmed by the calculated value of the non-Gaussian parameter $\alpha(t)$, which for dmim$^+$/Cl$^-$ components is equal to 1.78. The time dependence of the non-Gaussian parameter of methanol in dmim$^+$/Cl$^-$ at $T = 400$ K has several features: the values of the non-Gaussian parameter of the methanol in dmim$^+$/Cl$^-$ at $T = 400$ K (Fig. 3) at $t < 25$ ps increase linearly with increasing time. At $t \sim 35$ ps, the value of $\alpha(t)$ reaches a maximum, indicating a violation of the dmim$^+$/Cl$^-$ dynamic

heterogeneity by the methanol molecule. This molecule inhibits the movement of cations and anions of dmim$^+$/Cl$^-$, and its motion mode is diffusive [39].

Because dimethylimidazolium chloride (dmim$^+$) has a melting point of 399 K [40], we can expect that at $T = 400$ K the average interaction energy between the components of the IL is quite large. In this case diffusion in dmim$^+$/Cl$^-$ is determined by activation jumps of the system's components (vibrational-hopping diffusion mechanism). In the intervals between jumps, the dmim$^+$/Cl$^-$ components oscillate near the equilibrium position. According to Frenkel's ideas [33], at a temperature close to the melting temperature, the characteristic time between jumps of a particle by distances comparable to inter-particle ones $\tau_0$ (relaxation time) significantly exceeds the characteristic period of particle oscillation. Therefore, the studied system should be considered as an almost harmonic oscillatory system with single-particle jumps. At the same time, when a particle oscillates between jumps once or twice, it is difficult to differentiate between the vibrational and vibrational-hopping mechanisms of particle motion. The analysis of correlation functions $F_s(\vec{q},t)$ clarifies this issue [41],

$$F_r(\vec{q},t) = \frac{1}{N}\left(\sum_{j=1}^{N} \exp\left[\vec{iq}\left(\vec{r}_j(t) - \vec{r}_j(0)\right)\right]\right) \tag{6}$$

where $\vec{q}$ is the wave vector. Indeed, the analysis of $F_s(\vec{q},t)$ (Fig. 4a) functions and their derivatives $\left(\dfrac{\partial^2 F_s(\vec{q},t)}{\partial t^2}\right)$ (Fig. 4b) can be used to study the features of particle motion modes in the dmim$^+$/Cl$^-$-methanol system. The behavior of the derivatives of the correlation functions $\left(\dfrac{\partial^2 F_s(\vec{q},t)}{\partial t^2}\right)$ of the dmim$^+$/Cl$^-$-methanol system components (Fig. 4b) confirms the assumption of a change in the mode of motion at $t \sim 5$ ps. It should be noted that the values of the derivatives $\left(\dfrac{\partial^2 F_s(\vec{q},t)}{\partial t^2}\right)$ for the Cl$^-$ anions and methanol molecules at $t > 10$ ps are identical. This confirms the assumption that, at $t \sim 10$ ps, stable systems that move in the complex are formed between the methanol and Cl$^-$ anions. At $t > 35$ ps,
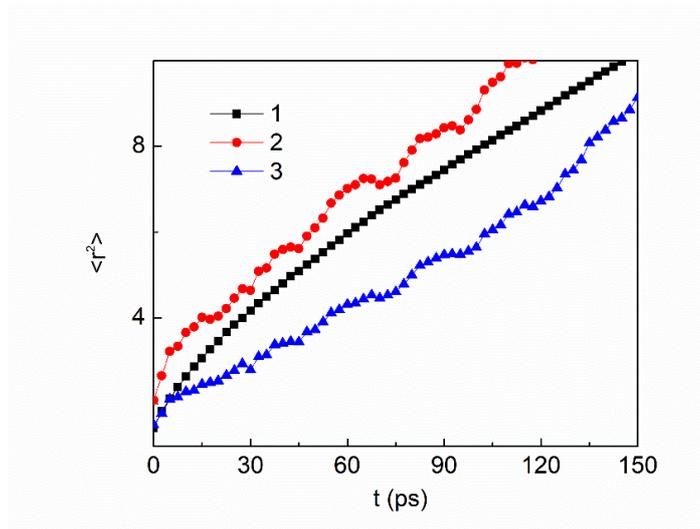
**Fig. 2.** The mean-square displacement $<r^2>$ of the components of the dmim$^+$/Cl$^-$-methanol system (1-dmim$^+$; 2-methanol; 3-Cl$^-$) at $T = 400$ K.
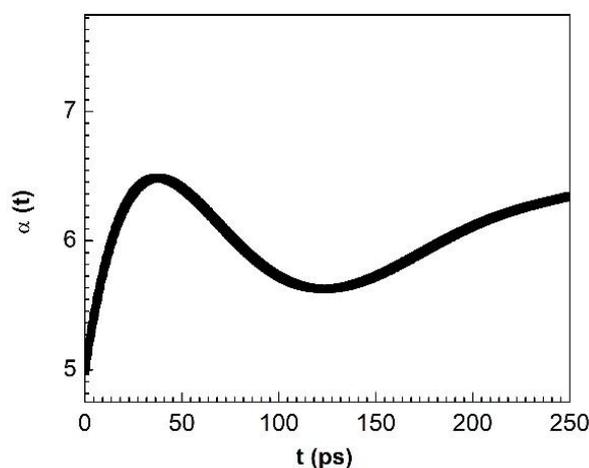


**Fig. 3.** Time dependence of the non-Gaussian parameter $\alpha(t)$ of methanol in dmim$^+$/Cl$^-$ at $T = 400$.

the values of the derivatives $\left( \dfrac{\partial^2 F_s(\vec{q},t)}{\partial t^2} \right)$ are identical for all components of the system. This result allows us to suggests that the motion mechanisms of all components of the system under consideration are the same over long time intervals $t > 35$ ps. Thus, at $t \geq 35$ ps, relaxation processes in the

system under consideration can be described within the framework of the α-relaxation model, which describes structural-dynamic processes in a liquid at relatively large times.

Based on the conclusions of Ref. [41], it can be assumed that for $t < 5$ ps, the motion of methanol occurs as the result of inelastic collisions with the dmim$^+$/Cl$^-$ components, as
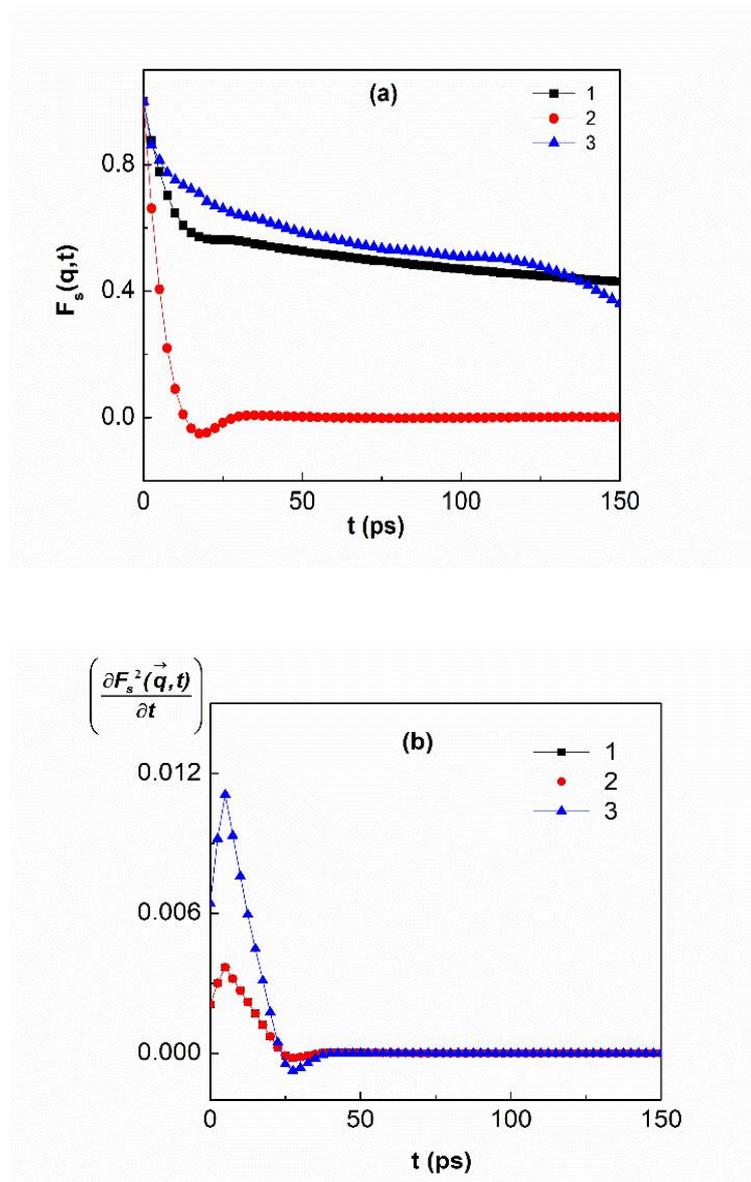
**Fig. 4.** Time dependence of correlation functions $F_s(\vec{q},t)$ (a) and its derivatives $\left( \dfrac{\partial^2 F_s(\vec{q},t)}{\partial t^2} \right)$ (b) for the system

dmim$^+$/Cl$^-$-methanol (1–dmim$^+$, 2–methanol, 3–Cl$^-$) at $T$ = 400 K.

well as jumps by a distance whose value coincides with the average distance between particles $a$. Near the melting temperature, the characteristic values of the parameter $a^2/D$ corresponds to the jump time of the molecules $\tau^*$, comparable with the time of one oscillation $\tau_0$. In this case, the relaxation time can be represented as the average time of

the jump by the distance $a$, the value of which can be determined using the equation [41]:

$$\tau \sim \frac{a^2}{6D} \tag{7}$$

It is important to understand that the value of the average

distance between particles $a$ is closely related to the size of the free space formed around the dissolved substance, and can be obtained from the analysis of the radial distribution functions RDF. The diffusion coefficient $D$ is calculated according to [30]:

$$D = \frac{1}{3}\int_0^\infty \langle V(0)V(t)\rangle dt \qquad (8)$$

where $\langle V(0)V(t)\rangle$ is a time-dependent velocity autocorrelation function.

It is found that the average value of the diffusion coefficient of the components in the system is: dmim + cations - $D_{dmim} = 0.06 \times 10^{-9}$ m$^2$ s$^{-1}$, anions - $D_{Cl} = 0.02 \times 10^{-9}$ m$^2$ s$^{-1}$, methanol in dmim$^+$/Cl$^-$ - $D_{met} = 0.09 \times 10^{-9}$ m$^2$ s$^{-1}$.

Now we take in to account the following facts. In a first approximation, methanol can be considered as a sphere with an effective radius $R \sim 1.4$ Å [42]. Then, according to the data from [43], the average distance between Cl$^-$ anions is $\sim 5.9$ Å, the average distance between the anion of Cl$^-$ and the cation of dmim$^+$ in the dmim$^+$/Cl$^-$-methanol system is $\sim 2.8$ Å, and the average distance between the dmim$^+$ cations and the alcohol molecule is $\sim 3.1$ Å. Accordingly, we can assume that free space is formed when methanol dissolves in dmim$^+$/Cl$^-$, the minimum radius of which is $\sim 2.8$ Å, and the inter-particle distance is $a \sim 8.3$ Å. According to Eq. (7), the jump time of the alcohol molecules in the dmim$^+$/Cl$^-$-system to the inter-particle distance is the same as the relaxation time of the system at $T = 400$ K, or $\sim 3.6$ ps for methanol. This indicates structural transformations in the system at times $t < 5$ ps. The diffusion of the methyl alcohol molecule in dmim$^+$/Cl$^-$ occurs due to inelastic collisions with the components of dmim$^+$/Cl$^-$ and jumps by inter-particle distances. The jump time of the alcohol molecule coincides with the relaxation time of the system based on dmim$^+$/Cl$^-$ at $T = 400$ K, and is about $\sim 3.6$ ps. The motion of an alcohol molecule in the dmim$^+$/Cl$^-$-system at these times can occur through deformation or breakdowns of the network of hydrogen bonds between the components of the IL, resulting in a rearrangement of the local liquid structure.

## CONCLUSIONS

The molecular dynamics method was used to study the structural and dynamic properties of the dmim$^+$/Cl$^-$-methanol system over a time interval of $\sim 150$ ps at $T = 400$ K. Model representations, based on the obtained data, are proposed to describe the relaxation processes. Consequently, we demonstrate that:

The establishment of thermodynamic equilibrium in the dmim$^+$/Cl$^-$-methanol system is associated with both short ($\beta$-relaxation) and relatively long relaxation processes.

$\beta$-Relaxation processes at $t < 5$ ps are accompanied by the rearrangement of the local structure of the dmim$^+$/Cl$^-$-methanol system. The relaxation time coincides with the jump time of the alcohol molecule by an inter-particle distance and amounts to $\sim 3.6$ ps. The motion of the methanol molecule in dmim$^+$/Cl$^-$ can occur through deformation or breaks of the network of hydrogen bonds between the IL components, leading to a rearrangement of the local liquid structure. The diffusion of methanol in dmim$^+$/Cl$^-$ occurs due to inelastic collisions with the components of dmim$^+$/Cl$^-$ and also to jumps to inter-particle distances.

At $t > 10$ ps, the motion of particles participating in ballistic collisions decreases, leading to the formation of chlorine-methanol syatems, as well as the existence of clusters of ionic liquid components. At $t \sim 35$ ps, the methanol molecule disrupts the dynamic heterogeneity of dmim$^+$/Cl$^-$ and inhibits the motion of the dmim$^+$/Cl$^-$ components. Thus, based on the analysis performed, it can be assumed that at $t \geq 35$ ps the dynamic processes in the system under study can be described in the framework of the relaxation model which describes the structurally dynamic processes in the liquid at relatively large times.

## ACKNOWLEDGMENTS

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