Adaptive resolution scheme for efficient hybrid atomistic-mesoscale molecular dynamics simulations of dense liquids

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The adaptive resolution scheme (AdResS) for efficient hybrid particle-based atomistic/mesoscale molecular dynamics (MD) simulations recently introduced by us, [J. Chem. Phys. 123, 224106 (2005)] is extended to high density molecular liquids with spherical boundaries between the atomistic and mesoscale regions. The key feature of this approach is that it allows for a dynamical change of the number of molecular degrees of freedom during the course of a MD simulation by an on-the-fly switching between the atomistic and mesoscopic levels of detail. Pressure and density variations occurring at the atomistic/mesoscale boundary in the original version are considerably reduced employing the improved methodology presented here.

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I. INTRODUCTION

Molecular liquids and soft matter are typical examples, where the interplay between different length scales determines the relevant properties of the system. The theoretical study of such systems using computer simulation techniques, which aim for a comprehensive understanding, therefore, requires a multiscale modeling approach to bridge between the various length and time scales involved. In order to efficiently address these problems we have recently introduced the adaptive resolution scheme (AdResS) for hybrid particle-based atomistic/mesoscale molecular dynamics (MD) simulations [1], which combines the merits of fully atomistic with those of the mesoscopic MD simulations. The unique feature that separates our new approach from other scale bridging particle-based simulations [2–4,8,9] is that it allows us to change the level of detail and hence the number of molecular degrees of freedom in the system on-the-fly during the course of the MD simulation. Particles and/or molecules can move freely from one resolution regime into the other. By such a dynamical switching between the atomistic and mesoscopic resolutions one has the option to treat only as many degrees of freedom as absolutely necessary for the problem considered. This approach is thus suited for molecular systems, where spatially localized domains with the required atomistic resolution exchange particles with the remainder of the system sufficiently described on the mesoscopic level of detail. For example, one could run a system on a mesoscale level and then, depending on some chosen criteria, zoom into some subdomain of the system, where a more detailed resolution would be required at a given instant. The applicability of the method is by no means limited to solely couple the atomistic and mesoscopic levels of detail but can also be employed to link two arbitrary mesoscopic domains with different levels of coarse graining. Extensions in this direction where more than two levels of resolution are treated are, in principle, straightforward in this context. Recently, a similar idea was followed within a Monte Carlo simulation [7]. Both schemes give the same molecular densities in both regimes. We here, however, especially focus on the molecular structure, which is not given in Ref. [7].

In Ref. [1] we have tested the method on the medium dense model liquid of model tetrahedral molecules where the atomistic region was separated from the coarse-grained domain by a flat boundary. This is the geometry one would apply, for example, in studies of liquids near (metal) surfaces [2–4,8,9], where close to the surface the detailed structure of the liquid is crucial, while farther away a more coarse-grained model is fully sufficient. For the case of a synthetic or biological macromolecule embedded in a solvent, see for example, Ref. [6], a spherical geometry is more appropriate with a spherically shaped atomistic region surrounded by a coarse-grained domain. Thus the first goal of this paper is to generalize the method from Ref. [1] to be also applicable for these kind of situations.

One can consider the resolution switching as a geometry induced first-order phase transition. Therefore, at equilibrium, boundary conditions analogous to two phase coexistence must hold implying that the chemical potentials, pressures, and temperatures in both regions with different levels of detail are the same. These conditions assure that there is no net flux of molecules between the two regions, which guarantees that the liquid is homogeneous across the simulation box as it is in the reference all-atom system. We demonstrated in Ref. [1] that when using our method any spurious unphysical net flux, resulting in a density difference between the two regimes, is avoided. We show in the present study that small (∼5%) pressure and density variations in the transition layer between the atomistic and coarse-grained regimes emerging as an artifact of the original scheme [1] can be reduced by a careful reparametrization of the effective pair potential in the transition layer.

We have also extended the method from medium to high (or regular) density liquids, where a tabulated effective pair potential must be used instead of the analytical one to correctly reproduce the equation of state of the reference all-atom system around the considered phase point [10].

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II. ALL-ATOM MODEL LIQUID

To test and validate the new approach to multiscale MD simulations we resort to the generic explicit (ex) model of a liquid of tetrahedral molecules as introduced in Ref. [1]. This model system mimics a typical soft matter system, e.g., a colloidal sphere system, liquid methane, etc. Each molecule in this model is composed of four equal atoms with mass \( m_0 \). Their size \( \sigma \) is fixed via the repulsive Weeks-Chandler-Andersen potential

\[
U_{\text{rep}}(r_{ij}) = \left\{ \begin{array}{ll}
4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} + \frac{1}{4} \right] & ; \quad r_{ij} \leq 2^{1/6} \sigma \\
0 & ; \quad r_{ij} > 2^{1/6} \sigma
\end{array} \right.
\]

with the cutoff at \( 2^{1/6} \sigma \). We use \( \sigma \) as a unit of length and \( \varepsilon \) as a unit of energy. Here \( r_{ij} \) is the distance between the atom \( i \) of the molecule \( \alpha \) and the atom \( j \) of the molecule \( \beta \). The neighboring atoms in a given molecule \( \alpha \) are connected by the finite extensible nonlinear elastic (FENE) bonds

\[
U_{\text{bond}}(r_{ij}) = \left\{ \begin{array}{ll}
-\frac{1}{2} k R_0^2 \ln \left[ 1 - \left( \frac{r_{ij}}{R_0} \right)^2 \right] & ; \quad r_{ij} \leq R_0 \\
\infty & ; \quad r_{ij} > R_0
\end{array} \right.
\]

with divergence length \( R_0 = 1.5 \sigma \) and stiffness \( k = 30 \varepsilon / \sigma^2 \).

III. COMPUTATIONAL METHOD

A. Adaptive resolution MD scheme (AdResS)

Our recently introduced AdResS [1] consists of two main steps. First, we map the fully atomic ex model to a coarse-grained (cg) mesoscopic model (in this specific case composed of a one-particle coarse-grained molecule with mass \( 4m_0 \)) and derive the effective pair potential \( U^{\text{cm}}(r) \) between coarse-grained molecules. We derive the effective cg potential in such a way that the center-of-mass radial distribution function (RDF\_cm) and pressure of the cg system match the corresponding RDF\_cm and pressure of the ex system at a given density and temperature [11]. For the effective pair potential derivation one can resort to various methods found in the literature, see, e.g., Refs. [10,12–14]. In order to avoid any density difference and net flux between the two regimes, the cg potentials have to be chosen such that the equations of state for the ex and cg systems coincide around the state point considered.

Second, we introduce the hybrid atomistic-mesoscopic (ex-cg) model system composed of explicit and coarse-grained molecules as presented in the Figs. 1(a) and 1(b). In the present study, the atomistic region, which is positioned at the center of the simulation box, has a spherical shape. It is surrounded by the coarse-grained domain, which is spread over the rest of the system with standard periodic boundary conditions. The two regions freely exchange molecules through a transition regime, where they change their resolution and their number of degrees of freedom accordingly as described in Ref. [1]. This interface region contains hybrid molecules, each of which is composed of the explicit atomistically resolved molecule with an additional massless center-of-mass particle serving as an interaction site. This transition, which has to be smooth for MD simulations, is governed by a weighting function \( w(r) \). The latter smoothly interpolates between the two regimes. For the present spherical geometry we adopt the function used before [1] for the case of the flat boundary, in the following functional form:

\[
w(r) = \left\{ \begin{array}{ll}
1 & ; \quad r_0 > r \geq 0 \\
0 & ; \quad r \geq r_0 + d \\
\cos^2 \left[ \frac{\pi}{2d} (r - r_0) \right] & ; \quad r_0 + d > r \geq r_0
\end{array} \right.
\]

where \( r_0 \) is the radius of the atomistic region and \( d \) the interface region width (see Fig. 2).

With this transition function, we couple the atomic and mesoscopic length scales via the ansatz for the total intermolecular force acting between the centers of mass of molecules \( \alpha \) and \( \beta \), as given below for the spherical geometry:

\[
\mathbf{F}_{\alpha\beta} = w(R_\alpha)w(R_\beta)\mathbf{F}_{\alpha\beta}^{\text{atom}} + [1 - w(R_\alpha)w(R_\beta)]\mathbf{F}_{\alpha\beta}^{\text{cm}},
\]

where

\[
\mathbf{F}_{\alpha\beta}^{\text{cm}} = -\frac{\partial U^{\text{cm}}}{\partial \mathbf{R}_{\alpha\beta}}.
\]

The force

\[
\mathbf{F}_{\alpha\beta}^{\text{atom}} = \sum_{i_{\alpha},j_{\beta}} \mathbf{F}_{i_{\alpha}j_{\beta}}^{\text{atom}}
\]

is the sum of all pair atom interactions between explicit atoms of the molecule \( \alpha \) and explicit atoms of the molecule \( \beta \).
different regimes molecules retain their linear momentum and efficiently equilibrate additional degrees of freedom.

As demonstrated in Ref. [1] for the case of the flat boundary between regions with different levels of detail using the method described above, at equilibrium, the boundary conditions similar to the two phase coexistence

\[ \mu_{\text{ex}} = \mu_{\text{cg}}, \quad p_{\text{ex}} = p_{\text{cg}}, \quad T_{\text{ex}} = T_{\text{cg}}, \]

are implicitly satisfied. Here \( \mu_{\text{ex}}, p_{\text{ex}}, T_{\text{ex}} \) and \( \mu_{\text{cg}}, p_{\text{cg}}, T_{\text{cg}} \) are the chemical potentials, pressures, and temperatures of the liquid in the atomistic and coarse-grained domains, respectively. The conditions (8) guarantee that there is no net flux of molecules between the atomistic and coarse-grained regions.

IV. MULTISCALE SIMULATION PROTOCOL

We carried out our hybrid multiscale simulations using the ESPResSo package [21], developed at our institute. We employed the replacement hybrid model system [1] and performed MD simulations with the Langevin thermostat integrating the Langevin equation

\[ \frac{d^2 r_i}{dt^2} = \frac{\partial U_{\text{atom}}}{\partial r_{i\alpha\beta}} - \frac{W_i(t)}{m_i}, \]

for each particle in the system, where \( m_i \) is the mass of the particle \( i \), \( F_i \) is the total force acting on the respective particle, \( \Gamma \) is a friction constant, and \( W_i \) is the random force of a heat bath [22]. The value of the friction constant is \( \Gamma = 0.5 \sigma^2 / \tau \), where \( \tau = (\varepsilon / m_i \sigma^2)^{-1/2} \). We sample the random force from a uniform distribution [23]. Periodic boundary conditions and the minimum image convention [24] are employed. For the integration a standard velocity Verlet algorithm with a \( \Delta t = 0.005 \tau \) time step was used. After warm-up and equilibration, trajectories of 75000 \( \tau \) were obtained, with configurations stored every 5 \( \tau \) time for analysis. This production runs are performed with a \( 10^6 \varepsilon / \sigma^2 \) force capping to prevent possible force singularities that could emerge due to overlaps with the neighboring molecules when a given molecule enters the interface layer from the coarse-grained side [1].

All MD simulations are performed at temperature \( T = \varepsilon / k_B \) and two molecular number densities \( \rho = \pi N / V = 0.1 / \sigma^3 \) and 0.175 / \( \sigma^3 \), with \( N \) being the number of molecules. In both cases \( n = 5000 \), corresponding to a cubic box size of \( a = 36.845 \sigma \) or 30.57 \( \sigma \) for the low and the high density, respectively. The molecules can be either the explicit, coarse-grained or hybrid. In the case of the all-atom system these molecular densities correspond to \( \rho = \pi N / V = 0.4 / \sigma^3 \) and 0.71 / \( \sigma^3 \) particle number densities, respectively, with \( N \) being the number of particles. To compare our model system densities with the Lennard-Jones liquid densities we use the same estimate for the excluded volume diameter of the coarse-grained molecule \( \sigma_{cg} \) as in Ref. [1], i.e., the distance, where the repulsive effective pair potential between the coarse-grained molecules in our simulations equals \( k_B T (\sigma_{cg} = 1.7 \sigma \) and \( \sigma_{cg} = 1.795 \sigma \) for the medium and high density liquids, respectively). The molecular number density \( \rho = 0.1 / \sigma^3 \) then corresponds to a medium dense liquid while the higher density \( \rho = 0.175 / \sigma^3 \).
correct.

V. RESULTS AND DISCUSSION

A. Mapping of the coarse-grained to the all-atom model

1. Medium dense liquid

We define the effective interactions between the coarse-grained molecules in the system at \( \rho = 0.1 \) and \( T = 1 \) using the effective pair potential \( U^{cm} \) derived in Ref. [1]. This is parameterized with the analytical Morse potential

\[
U^{cm}(r) = \gamma_1 \exp[-(k_1 r - r_c^1)]^2
\]

with parameters \( \gamma_1 = 0.105, \ k_1 = 2.2, \ r_c^1 = 2.31 \), and cutoff at \( r_c^1 \). The effective potential given by Eq. (10) is determined in such a way that the cg system reproduces the structure and the pressure of the reference ex system at the corresponding state point.

Our coarse-graining procedure does not incorporate the information about the energy fluctuations in the system. To compare the latter for the ex and cg systems we calculated the heat capacity of the respective systems formally defined as

\[
C_V = \frac{\langle \partial U / \partial T \rangle}{\langle E - \langle E \rangle \rangle^2} T^2
\]

where \( U = \langle E \rangle \) and \( E \) are the internal and total energies of the system, respectively. The brackets \( \langle \rangle \) denote the time average. The values of the heat capacities per molecule are \( C_V^{ex} \approx 0.4 \pm 0.03 \) and \( C_V^{cg} \approx 2.0 \pm 0.1 \) for the ex and cg systems, respectively. Their ratio \( C_V^{ex}/C_V^{cg} \approx 4.7 \), close to 4. In general, the heat capacity is proportional to the number of degrees of freedom in the system. This number is 4 times higher in the ex than in the cg system (an explicit molecule has 3 translational, 3 rotational, and 6 vibrational degrees of freedom compared to only 3 translational degrees of freedom of a coarse-grained molecule). For the noninteracting molecules the ratio \( C_V^{ex}/C_V^{cg} \) would therefore be exactly 4. This is not the case for the liquid due to the contribution of the intermolecular interaction potential to the internal energy of the liquid. We have also computed the respective \( C_V^{cs} \) using a smaller time step \( \Delta t = 0.0025 \) and/or smaller friction constant \( \Gamma = 0.25 \) and obtained similar values (within the computational error) indicating that our simulation protocol is correct.

2. High density liquid

A general feature of the effective pair potentials is that they are density and temperature dependent [27]. Therefore, one can reproduce the equation of state of a given all-atom system only at a certain range around the state point of interest by using an appropriate coarse-grained model with a chosen effective pair potential. In the study presented in Ref. [1] we were able to reproduce the equation of state of the ex system at \( T = 1 \) and densities up to \( \rho = 0.125 \) exploiting the cg model with the analytical effective pair potential given by Eq. (10). To also reproduce the respective equation of state, i.e., the structure and pressure of the ex system, at a high density of \( \rho = 0.175 \) that corresponds to a dense Lennard-Jones liquid we have to resort to tabulated numerical potential.

We derive the effective pair potential using the iterative Boltzmann inversion [12]. We use the potential given by Eq. (10) as the initial guess \( U_{tab}^{cm} \) for the effective pair potential of the cg system at \( \rho = 0.175 \) and \( T = 1 \). This potential is then further optimized via the iterative procedure

\[
U_{tab,k+1}^{cm} = U_{tab,k}^{cm} + T \ln \frac{g_{k}^{cm}(r)}{g_{ex}^{cm}(r)},
\]

where \( g_{k}^{cm}(r) \) and \( g_{ex}^{cm}(r) \) are the effective pair potential and corresponding RDF cm at the kth iteration.

In order to also match the pressure of the respective model system we add a linear correction term

\[
\Delta U^{cm} = U_0 \left( 1 - \frac{r}{r_c^1} \right),
\]

which vanishes at \( \Delta U^{cm}(r_c^1) = 0 \) and has \( U_0 = \Delta U^{cm}(r = 0) \) as the only parameter [10]. By the correction given by Eq. (13) we add a weak constant force to the effective force in such a way that the total effective force and potential are zero at the cutoff \( r_c^1 \). The latter is set to 3.5 to match the RDF cm up to the second maximum. Depending on the pressure in the current iteration being above or below the target value of the reference ex system, \( U_0 \) is negative or positive. The pressure correction Eq. (13) acts mostly on the long-range part of the pair interactions. In contrast, the structure of the system is almost completely determined by the short-range part of the pair interactions [28].

In Fig. 3(a) we present the tabulated numerical effective pair potential \( U_{tab}^{cm}(r) \) obtained after 5 iterations with \( U_0 = 0.22 \) followed by another 5 iterations with \( U_0 = 0.1 \). The RDF cm and tabulated potential \( U_{tab}^{cm}(r) \) are calculated with \( \Delta r = 0.01 \). Between these points we use a linear interpolation for the potential and force evaluation. For the RDF cm calculation we use the centers of mass of all the molecules in the simulation box.

The tabulated numerical effective pair potential \( U_{tab}^{cm}(r) \) for \( \rho = 0.175 \) is softer than the corresponding effective pair potential given by Eq. (10) as can be noticed from Fig. 3(a). It also exhibits a very shallow negative minimum despite the fact that all the interactions in the all-atom system are purely repulsive. This many-body effect here arises from the pressure correction defined by Eq. (13).

In Fig. 3(b) are depicted RDF cm of the ex and cg systems at \( \rho = 0.175 \) and \( T = 1 \). Although due to facilitated molecular rotations in our model liquid the height of the first maximum in the RDF cm of the ex system is lower as in typical highly dense liquids the number of nearest neighbors up to the first minimum at \( r = 2.625 \) is 12.83, a typical number for a highly
correlated liquid. This shows that the density of our model liquid indeed corresponds to a highly dense Lennard-Jones liquid. The RDF of the cg system using the tabulated effective potential for defining the effective interactions in the system matches to within line thickness with the reference RDF of the ex system.

As a merit function of the evaluated RDFs we introduce the penalty function defined as

$$f_p = \int \left[ g^{ex}(r) - g^{cm}(r) \right]^2 \exp(-r)dr,$$

where $g^{ex}$, which is taken as a reference, is the RDF of the ex system [1,12]. The RDFs are calculated in the range $r \in [0, 5]$ with $\Delta r = 0.05$.

In Table I we give the values of $f_p$ and average pressures of the respective systems. First, we can notice from the results in Table I that the value of $f_p$ for the cg system is even lower as for the medium dense liquid with $\rho = 0.1$ using the effective potential given by Eq. (10) (see the caption of Table II). This indicates that by using the tabulated numerical effective potentials one can better reproduce the structure of the reference all-atom system than by using the analytical potentials. Second, using the linear correction term Eq. (13) one can match the pressures in the cg system with the reference value of the all-atom model system.

The equations of state for ex and cg systems using the tabulated effective potential for the cg system at $\rho = 0.175$ and $T = 1$. Shown is also $U^{cm}(r)$, which holds for $\rho = 0.1$ as given by Eq. (10) for comparison. (b) RDFs of the ex and cg systems at $\rho = 0.175$ and $T = 1$. The RDFs match to the line-thickness.

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**TABLE I.** Penalty function $f_p$ defined by Eq. (14) and the average pressure $p$ for ex-cg systems at $\rho = 0.175$ and $T = 1$. The corresponding values of $f_p$ and $p$ are taken from Ref. [1].

<table>
<thead>
<tr>
<th>System</th>
<th>$f_p \times 10^3$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ex</td>
<td>0</td>
<td>1.99±0.02</td>
</tr>
<tr>
<td>cg</td>
<td>0.0262</td>
<td>1.98±0.02</td>
</tr>
</tbody>
</table>

**TABLE II.** Penalty function $f_p$ defined by Eq. (14) and the average pressure $p$ for ex-cg systems at $\rho = 0.175$ and $T = 1$. The RDFs match to the line-thickness.

<table>
<thead>
<tr>
<th>$r_0$</th>
<th>$f_p \times 10^3$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0^{ex}$</td>
<td>0</td>
<td>0.379±0.009</td>
</tr>
<tr>
<td>$0^{cg}$</td>
<td>0.2067</td>
<td>0.378±0.004</td>
</tr>
<tr>
<td>6.0</td>
<td>0.2020</td>
<td>0.379±0.003</td>
</tr>
<tr>
<td>7.0</td>
<td>0.1961</td>
<td>0.379±0.002</td>
</tr>
<tr>
<td>8.0</td>
<td>0.1925</td>
<td>0.379±0.003</td>
</tr>
<tr>
<td>9.0</td>
<td>0.1909</td>
<td>0.380±0.004</td>
</tr>
<tr>
<td>10.0</td>
<td>0.1837</td>
<td>0.380±0.004</td>
</tr>
<tr>
<td>11.0</td>
<td>0.1772</td>
<td>0.380±0.004</td>
</tr>
<tr>
<td>12.0</td>
<td>0.1729</td>
<td>0.380±0.006</td>
</tr>
<tr>
<td>13.0</td>
<td>0.1603</td>
<td>0.381±0.003</td>
</tr>
<tr>
<td>14.0</td>
<td>0.1535</td>
<td>0.382±0.004</td>
</tr>
<tr>
<td>15.0</td>
<td>0.1408</td>
<td>0.383±0.006</td>
</tr>
</tbody>
</table>

**FIG. 3.** (a) The tabulated effective potential $U^{cm}_{\text{tab}}(r)$ for the cg system at $\rho = 0.175$ and $T = 1$. Shown is also $U^{cm}(r)$, which holds for $\rho = 0.1$ as given by Eq. (10) for comparison. (b) RDFs of the ex and cg systems at $\rho = 0.175$ and $T = 1$. The RDFs match to the line-thickness.

**FIG. 4.** Equations of state at $T = 1$ for the ex and cg systems using the tabulated effective potential $U^{cm}_{\text{tab}}(r)$. Shown is the pressure $p$ as a function of the number density $\rho$ of the system.


To validate the results of AdResS we compare the computed statistical properties of the hybrid ex-cg system, as introduced in Sec. III, with the corresponding properties of the ex system.

In Fig. 5 we depict RDF<sub>cm</sub> of the ex and ex-cg systems at \( \rho = 0.1 \) and \( T = 1 \). Since the AdResS gives acceptable results for the interface region with widths larger than the maximal range of interaction \([1]\) we set in this study \( d = 2.5 \). Shown is the case where the radius of the all-atom region is \( r_0 = 12.0 \). The RDF<sub>cm</sub> of the ex-cg system matches up to a given accuracy of our parametrization to the RDF<sub>cm</sub> of the reference ex system indicating that the AdResS accurately reproduces the structure also in the case of the spherical shaped regions with a different level of detail. This is even more clear from the results given in Table II, where the \( f_p \) and average pressure are given as a functions of \( r_0 \) for the ex-cg system.

Using Eq. (11) we also computed the heat capacities per molecule \( C_V^{ex} \) and \( C_V^{cg} \) for the high density liquid. The corresponding values are \( C_V^{ex} = 9.5 \pm 0.5 \) and \( C_V^{cg} = 2.4 \pm 0.1 \), respectively. Their ratio \( C_V^{ex}/C_V^{cg} = 4 \) is as in the case of the medium dense liquid close to 4.

B. Hybrid atomistic/mesoscale (ex-cg) system

1. Medium dense liquid

Using Eq. (11) we also computed the heat capacities per molecule \( C_V^{ex} \) and \( C_V^{cg} \) for the high density liquid. The corresponding values are \( C_V^{ex} = 9.5 \pm 0.5 \) and \( C_V^{cg} = 2.4 \pm 0.1 \), respectively. Their ratio \( C_V^{ex}/C_V^{cg} = 4 \) is as in the case of the medium dense liquid close to 4.

Using the \( U_{int}^{ex} \) for defining the effective pair interactions in the system we have computed as in the case of a

![Graph](image-url)

**FIG. 5.** RDF<sub>cm</sub> of the ex and ex-cg systems with \( r_0 = 12.0 \) and \( d = 2.5 \) at \( \rho = 0.1 \) and \( T = 1 \).

![Graph](image-url)

**FIG. 6.** Time evolution of the number of molecules in the ex, cg, and interface (int) regions of the ex-cg system with \( r_0 = 12.0 \) and \( d = 2.5 \) at \( \rho = 0.1 \) and \( T = 1 \). The average numbers of molecules in the ex, cg, and int regions are \( 724 \pm 35, 3736 \pm 53, \) and \( 539 \pm 32 \), respectively.

A finite size effect and should diminish with the growing system size when the size of the transition regime becomes negligible in comparison to the rest of the system.

The structure of the underlying ex system is accurately reproduced using the AdResS because the number of molecules in the interface regime is small in comparison to the rest of the system as can be observed from the results in Fig. 6 where the time evolution of number of molecules in all three different regimes of hybrid systems with \( r_0 = 12.0 \) and \( d = 2.5 \) is displayed. The theoretical estimates, which are in a good agreement with the simulation averages, for the numbers of molecules in different regions of a homogeneous liquid are \( n_{ex} = \rho V_{ex} = 723 \), \( n_{cg} = \rho V_{cg} = 3724 \), and \( n_{int} = \rho V_{int} = 553 \), where \( V_{ex}, V_{cg}, \) and \( V_{int} \) are the volume sizes of ex, cg, and interface (int) regions, respectively. The number of molecules in the all-atom and interface domains is much lower than in the cg region as will also be the case in the MD simulations of realistic soft matter systems in order to reduce the computational costs. The results in Fig. 6 demonstrate that also for the case of the spherical shape of the atomistic and coarse-grained regimes the AdResS guarantees that the chemical potentials at the boundary between regions with different levels of detail are equal as required by Eq. (8).

This is further supported by the results presented in Fig. 7, in which we present the normalized radial number density profiles of the ex-cg system with \( r_0 = 6.0 \) and \( r_0 = 12.0 \). One can observe that the density in the ex and cg regimes of the ex-cg system is equal to the reference density \( \rho_0 = 0.1 \). As in the example of flat boundary between different regimes \([1]\), the density oscillates around the reference value with an amplitude of approximately 0.05\( \rho \) in the interface region of the ex-cg system.

2. High density liquid

Using the \( U_{int}^{ex} \) for defining the effective pair interactions in the system we have computed as in the case of a
medium dense liquid with $\rho=0.1$ the RDFs, $f_p$, average pressure, time evolution of number of molecules in the different regimes in the system, and the density profiles of the ex-cg system at $\rho=0.175$ and $T=1$, as presented in Fig. 8, Table III, and Figs. 9 and 10, respectively. Although the range of the effective pair interactions is here 3.5, as one can observe from the curves in Fig. 3, the interactions are so small for the distances beyond 2.5 that we set $d=2.5$ also in this case in order to minimize the size of the transition regime.

The conclusions on the basis of results in Fig. 8, Table III, and Fig. 9 are the same as in the case of the medium dense liquid with $\rho=0.1$, i.e., the AdResS accurately reproduces the statistical properties of the reference ex system. Actually, the reproduction of the RDFs of the reference ex system is in this case even better due to the usage of the tabulated numerical effective pair potential. Note, however, that here $f_p$ reported in Table III goes up with $r_0$ in contrast to the case of the medium dense liquid. This is because the amplitude of density variations in the transition regime increases in comparison with the medium dense liquid as it can be observed from the density profile of the ex-cg system presented in Figs. 10(a) and 10(b), respectively. The increased density fluctuations slightly affect the quality of the computed RDFs for this moderate system size. Since the size of the transition regime, as already explained, grows with $r_0$ the value $f_p$ goes up with $r_0$. The amplitude of density oscillations in the transition regime increases because the interac-

<table>
<thead>
<tr>
<th>$r_0$</th>
<th>$f_p \times 10^3$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0</td>
<td>0.0246</td>
<td>1.99±0.01</td>
</tr>
<tr>
<td>7.0</td>
<td>0.0263</td>
<td>1.99±0.02</td>
</tr>
<tr>
<td>8.0</td>
<td>0.0273</td>
<td>1.99±0.02</td>
</tr>
<tr>
<td>9.0</td>
<td>0.0293</td>
<td>2.00±0.01</td>
</tr>
<tr>
<td>10.0</td>
<td>0.0350</td>
<td>2.01±0.02</td>
</tr>
<tr>
<td>11.0</td>
<td>0.0400</td>
<td>2.01±0.02</td>
</tr>
<tr>
<td>12.0</td>
<td>0.0488</td>
<td>2.02±0.02</td>
</tr>
</tbody>
</table>

FIG. 7. The normalized radial number density profiles of the ex-cg system at $\rho=0.1$ and $T=1$. (a) $r_0=6.0$, (b) $r_0=12.0$. The vertical lines denote the boundaries of the interface region with $d=2.5$.

FIG. 8. RDFs of the ex and ex-cg, and systems with $r_0=6.0$ and $d=2.5$ at $\rho=0.175$ and $T=1$.

FIG. 9. Time evolution of the number of molecules in different regimes of the ex-cg system with $r_0=11.0$ and $d=2.5$ at $\rho=0.175$ and $T=1$. The theoretical predictions for the numbers of molecules in different regions of a homogeneous liquid are $n_{ex}=975$, $n_{cg}=3197$, and $n_{int}=828$. The corresponding simulation averages in the ex, cg, and interface (int) regions are 979±31, 3210±33, and 809±26, respectively.
slightly different state point than the \textit{ex} and \textit{cg} systems. This causes the pressure and density variations in the interface layer as evident from Figs. 7 and 10.

Here, we correct for this by a reparametrization of the effective pair potential in the system composed of exclusively hybrid molecules with the constant \( w = \frac{1}{2} \) over the whole system. In the definition of intermolecular forces in the hybrid atomistic/mesoscale system, Eq. (4), we then replace the expression for the effective pair force given by Eq. (5) with

\[
F_{\alpha\beta}^{cm} = s[w(R_{\alpha})w(R_{\beta})]F_{\alpha\beta}^{ex} + (1 - s[w(R_{\alpha})w(R_{\beta})])F_{\alpha\beta}^{cg},
\]

where the function \( s \in [0,1] \) is defined as

\[
s[x] = 4\left(\frac{x}{2}\right)^2,
\]

so that \( s[0] = 1 \), \( s[1] = 1 \), and \( s[\frac{1}{2}] = 0 \). The force \( F_{\alpha\beta}^{cm} \) is the “original” effective pair force between molecules \( \alpha \) and \( \beta \) defined by the effective pair potential, which is obtained by mapping the \textit{cg} model to the \textit{ex} model as explained in Sec. V A. The “interface correction (ic)” force \( F_{\alpha\beta}^{cm} \) is the effective pair force between molecules \( \alpha \) and \( \beta \) defined by the effective pair potential, which is obtained by mapping the hybrid model system composed of exclusively hybrid molecules with \( w = \frac{1}{2} \) to the \textit{ex} model system. The force \( F_{\alpha\beta}^{cm} \) given by Eq. (15) is thus slightly different than \( F_{\alpha\beta}^{cm} \) used in the original scheme. The even function given by Eq. (16) is the simplest symmetrical choice to correct the effective pair interactions in the transition regime while leaving the (correct) effective pair interactions in the coarse-grained and atomistic regimes unchanged.

Further improvement could be achieved by additional effective potential derivations obtained by mapping the hybrid systems composed of exclusively the hybrid molecules with different constant values of \( w \) to the \textit{ex} system and then use a table for each value of \( w(R_{\alpha})w(R_{\beta}) \) for the effective pair interactions calculation. This would soften the resolution switching in a similar way as it is done in the thermodynamic integration [29] for the free energy difference calculations. The price to pay are the additional force calculations of hybrid molecules with the neighboring molecules. Thus, there is the trade-off between the accuracy in the transition regime and computational costs of the method.

C. Interface pressure correction

Intuitively, a normalized linear combination of explicit and coarse-grained forces given by the ansatz in Eq. (4) that defines the interactions of hybrid molecules in the transition regime should yield an effective interaction that gives a pressure that is close to the respective pressure values in the \textit{ex} and \textit{cg} systems. However, as found in Ref. [1], the pressure in a system containing exclusively the hybrid molecules with the constant \( w \neq 0,1 \) is slightly dependent on the \( w \) value, i.e., the ratio between the explicit-explicit and mesoscale-mesoscale interactions. This indicates that each system composed of exclusively the hybrid molecules with a different constant \( w \) is due to different effective interactions at a

\[
U_{ic}^{cm}(r) = \gamma_c(1 - \exp[-\kappa(r-r_c)])^2,
\]

with the same parameters as the effective potential given by Eq. (10) except from \( \gamma_c = 0.045 \).

FIG. 10. The normalized radial number density profiles of the \textit{ex-cg} system at \( \rho = 0.175 \) and \( T = 1 \). (a) \( r_0 = 6.0 \). (b) \( r_0 = 11.0 \). The vertical lines denote the boundaries of the interface region with \( d = 2.5 \).
The effective potentials given by Eqs. (10) and (17) are depicted in the inset of Fig. 11. The interactions defined by the effective potential $U^w_{cm}(r)$ have the same interaction range as the effective interactions determined by $U^m(r)$, yet they are weaker at short distances. This is to compensate for too strong interactions between molecules in the interface region arising from the normalized linear combination of the atomic and effective pair forces using the ansatz given by Eq. (4).

In Fig. 11 we present RDFs of $ex$, $ex$-$cg$($w=\frac{1}{2}$), and $ex$-$cg$($w=\frac{1}{2}$)$_{ic}$ systems at $\rho=0.1$ and $T=1$. The results demonstrate that by using the effective pair potential given by Eq. (10) for a calculation of the effective pair interactions in the $ex$-$cg$($w=\frac{1}{2}$) system, which contains exclusively the hybrid molecules with $w=\frac{1}{2}$, we cannot reproduce satisfactorily the structure of the reference all-atom system. The coordination at the first peak is overestimated in the $ex$-$cg$($w=\frac{1}{2}$) system using this potential. In contrast, using the effective potential given by Eq. (17) for a calculation of the effective pair interactions in the $ex$-$cg$($w=\frac{1}{2}$)$_{ic}$ system we can again reproduce satisfactorily the structure of the reference all-atom system.

This observation can be further confirmed by the corresponding values of $f_p$ defined by Eq. (14). The values of the $f_p$ for $ex$-$cg$($w=\frac{1}{2}$), and $ex$-$cg$($w=\frac{1}{2}$)$_{ic}$ systems are given in Table IV. The results clearly demonstrate that using the corrected effective potential from Eq. (17) improves the structure in the $ex$-$cg$($w=\frac{1}{2}$)$_{ic}$ system.

In order that the equations of state of the $ex$-$cg$($w=\frac{1}{2}$)$_{ic}$ and $ex$ systems coincide around the state point at $\rho=0.1$ and $T=1$.

<table>
<thead>
<tr>
<th>Table IV. Penalty function $f_p$ defined by Eq. (14) and average pressure $p$ for $ex$-$cg$($w=\frac{1}{2}$) and $ex$-$cg$($w=\frac{1}{2}$)$_{ic}$ systems at $\rho=0.1$ and $T=1$.</th>
</tr>
</thead>
<tbody>
<tr>
<td>System</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>$ex$-$cg$($w=\frac{1}{2}$)</td>
</tr>
<tr>
<td>$ex$-$cg$($w=\frac{1}{2}$)$_{ic}$</td>
</tr>
</tbody>
</table>

TABLE V. Penalty function $f_p$ defined by Eq. (14) and average pressure $p$ for the $ex$-$cg$($w=\frac{1}{2}$)$_{ic}$ system at $\rho=0.1$ and $T=1$ as a function of $r_0$.

<table>
<thead>
<tr>
<th>$r_0$</th>
<th>$f_p \times 10^3$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0</td>
<td>0.1923</td>
<td>0.378±0.004</td>
</tr>
<tr>
<td>7.0</td>
<td>0.1878</td>
<td>0.378±0.004</td>
</tr>
<tr>
<td>8.0</td>
<td>0.1842</td>
<td>0.378±0.001</td>
</tr>
<tr>
<td>9.0</td>
<td>0.1731</td>
<td>0.378±0.004</td>
</tr>
<tr>
<td>10.0</td>
<td>0.1684</td>
<td>0.378±0.003</td>
</tr>
<tr>
<td>11.0</td>
<td>0.1578</td>
<td>0.379±0.005</td>
</tr>
<tr>
<td>12.0</td>
<td>0.1464</td>
<td>0.379±0.005</td>
</tr>
<tr>
<td>13.0</td>
<td>0.1316</td>
<td>0.379±0.004</td>
</tr>
<tr>
<td>14.0</td>
<td>0.1168</td>
<td>0.378±0.005</td>
</tr>
<tr>
<td>15.0</td>
<td>0.1051</td>
<td>0.379±0.006</td>
</tr>
</tbody>
</table>

$T=1$ the pressures of both systems must also be the same at this phase point. The corresponding pressure values are also reported in Table IV. We can see that the pressure in the $ex$-$cg$($w=\frac{1}{2}$)$_{ic}$ system with the applied pressure correction as given by Eq. (15) is much closer to the desired value of the underlying $ex$ system than this is the case for the $ex$-$cg$($w=\frac{1}{2}$) system without this correction.

In Table V we give the $f_p$ and average pressure as a function of $r_0$ for the $ex$-$cg$($w=\frac{1}{2}$)$_{ic}$ system. The latter is the hybrid atomistic/mesoscale system, described in Sec. III, where the interface pressure correction according to Eq. (15) is employed.

The results in Table V demonstrate that the RDFs of the $ex$-$cg$($w=\frac{1}{2}$)$_{ic}$ system match up with the RDFs of the reference $ex$ system. This shows that the AdResS accurately reproduces the structure also with the pressure correction applied. As in the case of the $ex$-$cg$ system with the growing radius of the all-atom region $r_0$, the values of $f_p$ are decreasing. In contrast to the the $ex$-$cg$ system the pressure also converges with the growing $r_0$ to the correct value of the reference $ex$ system, indicating that the pressure correction given by Eq. (15) successfully removes this artifact of the original scheme already for moderate system sizes.

The average numbers of molecules in the $ex$, $cg$, and interface (int) regions of the $ex$-$cg$($w=\frac{1}{2}$)$_{ic}$ system with $r_0=12.0$ are 722±25, 3726±41, and 552±24, respectively. These values are in agreement with the corresponding results for the $ex$-$cg$ system with $r_0=12.0$ given in Fig. 6. We demonstrated in Ref. [1] for the flat boundary geometry that molecules can diffuse freely across the interface layer of the $ex$-$cg$ system despite the pressure and density oscillation occurring in that layer. Hence, the agreement between molecular number fluctuations in $ex$-$cg$ and $ex$-$cg$($w=\frac{1}{2}$)$_{ic}$ systems indicates that the interface pressure correction given by Eq. (15) does not influence the diffusion across the interface region.

The normalized radial density profile for the $ex$-$cg$($w=\frac{1}{2}$)$_{ic}$ system with $r_0=12.0$ at $\rho=0.1$, and $T=1$ is shown in Fig. 12. We can see that the oscillation amplitude is considerably reduced exploiting the pressure correction given by Eq. (15) leading to the correct pressure in the system. Note that we could reduce the density oscillations in the transition regime even
2. High Density Liquid

We derive the effective pair potential $U^\text{cm}_{\text{lab}}(r)$ by mapping the $\text{ex-}cg[w=\frac{1}{2}]$ system at $\rho=0.175$ and $T=1$ to the corresponding $\text{ex}$ system using the iterative Boltzmann inversion given by Eqs. (12) and (13) with the same parameters as for the derivation of the tabulated effective potential $U^\text{cm}_{\text{tab}}(r)$ for the $cg$ system at $\rho=0.175$ and $T=1$. The effective pair potential defined by Eq. (17) is used as the initial guess for the iteration.

The tabulated numerical effective pair potential $U^\text{cm}_{\text{lab}}(r)$ obtained after 5 iterations with $U_0=0.2$ followed by another 4 iterations with $U_0=0.1$ is depicted in the inset of Fig. 13. As for the medium dense liquid $U^\text{cm}_{\text{lab}}(r)$ is softer than further as explained in Sec. V C. This might, in general, not even be necessary since the interface region will represent a minor portion of the system in MD simulations of the realistic soft matter systems.

![Graph showing RDF of the system](image)

FIG. 13. RDFs of the $\text{ex}$, $\text{ex-}cg[w=\frac{1}{2}]$, and $\text{ex-}cg[w=\frac{1}{2}]_\text{ic}$ systems at $\rho=0.175$ and $T=1$. The RDFs of the $\text{ex}$ and $\text{ex-}cg[w=\frac{1}{2}]_\text{ic}$ systems match within the line thickness. In the inset the corresponding corrected effective pair potential $U^\text{cm}_{\text{lab}}(r)$ and the effective pair potential $U^\text{cm}_{\text{lab}}(r)$ are shown.

![Graph showing RDF of the system](image)

FIG. 12. The normalized radial number density profile of the $\text{ex-}cg_\text{ic}$ system with $r_0=12.0$ at $\rho=0.1$ and $T=1$. The vertical lines denote the boundaries of the interface region with $d=2.5$.

### Table VI. Penalty function $f_p$ defined by Eq. (14) and average pressure $p$ for $\text{ex-}cg[w=\frac{1}{2}]$ and $\text{ex-}cg[w=\frac{1}{2}]_\text{ic}$ systems at $\rho=0.175$ and $T=1$.

<table>
<thead>
<tr>
<th>System</th>
<th>$f_p \times 10^3$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{ex-}cg[w=\frac{1}{2}]$</td>
<td>5.5716</td>
<td>2.51±0.02</td>
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<tr>
<td>$\text{ex-}cg[w=\frac{1}{2}]_\text{ic}$</td>
<td>0.0137</td>
<td>1.98±0.02</td>
</tr>
</tbody>
</table>

$U^\text{cm}_{\text{lab}}(r)$. The RDFs of the $\text{ex}$, $\text{ex-}cg[w=\frac{1}{2}]$, and $\text{ex-}cg[w=\frac{1}{2}]_\text{ic}$ are shown in Fig. 13.

Similarly to the system with $\rho=0.1$ the agreement for the $\text{ex-}cg[w=\frac{1}{2}]$ system, in which $U^\text{cm}_{\text{lab}}(r)$ is used to define the effective interactions between molecules, is worse. These observations are in agreement with the results given in Table VI, where we give $f_p$ and average pressures of the respective systems. The pressure in the $\text{ex-}cg[w=\frac{1}{2}]$ system is as in the case of the system with $\rho=0.1$ overestimated. However, we can correct for this artifact using the interface pressure correction according to Eq. (15) and $U^\text{cm}_{\text{lab}}(r)$ for computing the interactions in the $\text{ex-}cg[w=\frac{1}{2}]_\text{ic}$ system.

The $f_p$ and the average pressure of the $\text{ex-}cg_\text{ic}$ system at $\rho=0.175$ and $T=1$ are given in Table VII.

From the results presented in Table VII we can see that the value of $f_p$ decreases with the growing $r_0$ while the average pressure corresponds to the value in the reference all-atom system. The statistical properties of the hybrid system employing the interface pressure correction given by Eq. (15) thus converge to the corresponding properties of the all-atom system by increasing the size of the all-atom regime as demanded from a working hybrid scheme.

Also for the high density liquid the average numbers of molecules in the $\text{ex}$, $\text{cg}$, and interface (int) regions of the $\text{ex-}cg_\text{ic}$ system with $r_0=11.0$, which are $976\pm20$, $3199\pm63$, and $823\pm21$, respectively, are in good agreement with the corresponding numbers of the $\text{ex-}cg$ system. In addition, we also computed the fluctuations and average numbers of molecules in the sphere with the center positioned in one of the corners of the simulation box. The corresponding values for the $\text{ex-}cg$ system are $982\pm13$, $3184\pm62$, and $832\pm26$ for the molecules with the radial distance $r$ from the corner of the simulation box such that $r_0>r\equiv0$, $r\equiv r_0+d$, and $r_0+d>r\equiv r_0$, respectively. The same values for the $\text{ex-}cg_{ic}$

### Table VII. Penalty function $f_p$ defined by Eq. (14) and average pressure $p$ for the $\text{ex-}cg_\text{ic}$ system at $\rho=0.175$ and $T=1$ as a function of $r_0$.

<table>
<thead>
<tr>
<th>$r_0$</th>
<th>$f_p \times 10^3$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0</td>
<td>0.0228</td>
<td>1.98±0.02</td>
</tr>
<tr>
<td>7.0</td>
<td>0.0230</td>
<td>1.98±0.02</td>
</tr>
<tr>
<td>8.0</td>
<td>0.0211</td>
<td>1.98±0.02</td>
</tr>
<tr>
<td>9.0</td>
<td>0.0198</td>
<td>1.98±0.01</td>
</tr>
<tr>
<td>10.0</td>
<td>0.0189</td>
<td>1.98±0.02</td>
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<tr>
<td>11.0</td>
<td>0.0165</td>
<td>1.98±0.02</td>
</tr>
<tr>
<td>12.0</td>
<td>0.0132</td>
<td>1.98±0.01</td>
</tr>
</tbody>
</table>
oscillations also in the case of the high density liquid. This
tion regime of the high density liquid. Furthermore, this also shows that
pressure correction given by Eq. (15) has a negligible effect on the
diffusion of molecules across the interface layer also for the high
density liquid. Furthermore, this also shows that the increased density
and pressure fluctuations in the transition regime of the high density
ex-cg system do not affect significantly the diffusion of molecules across
the interface, so that the molecules can freely move across between
the all-atom and mesoscale regimes.

Finally, in Fig. 14 we present the normalized radial density
profile for the ex-cg system with \( r_0 = 11.0 \) at \( \rho = 0.175 \) and
\( T = 1 \). By comparing the density profile in Fig. 14 with its
counterpart for the ex-cg system shown in Fig. 10 we can conclude
that by using the interface pressure correction given by Eq. (15) we
can considerably reduce the density oscillations also in the case of the high density liquid. This demonstrates the reliability of our approach.

VI. CONCLUSIONS

In this work we have extended the applicability of the
adaptive resolution MD scheme (AdResS) introduced in Ref.
[1], that allows us to switch the level of detail on-the-fly
during the course of a MD simulation, to the case of the
spherical geometry where the atomistic region is in the cen-
ter of the simulation box surrounded by the mesoscopic
region. This situation is appropriate for simulations of biologi-
cal macromolecules embedded in a solvent. As a model
system we have employed a liquid of tetrahedral molecules,
which we had introduced in Ref. [1]. Next, we have managed
to reduce the pressure and density variations that occurred at
the interface region between the atomistic and mesoscopic
regimes as an artifact of the original method. We achieve that
by reparametrizing the effective pair potential for interac-
tions of the hybrid molecules in the interface region. Finally,
we have also tested the new method on a high density liquid
with the density corresponding to the high density Lennard-
Jones liquid. In contrast to the study presented in Ref. [1] we
have here resorted to the tabulated numerical effective poten-
tials that are able to reproduce the structure of the reference
all-atom system with the higher accuracy than the analytical
counterparts. The simulation results indicate that the AdResS
accurately reproduces the statistical properties of the refer-
ence all-atom system regardless of the geometry of the re-
gions with different levels of detail and regardless of the
density considered. In principle, one could derive the full
density dependency of the effective potential to cover the
whole density range but this was not in the focus here. Our
method, which enables us to cover much longer length scales
than the conventional all-atom MD simulation, can also be
combined with the hybrid atomistic-continuum MD simula-
tion methods for fluids, see, e.g., Refs. [30–34], to bridge
over an even larger range of length scales in such systems.
Our long term aim is to extend this methodology from mol-
ecular liquids to macromolecular systems in a solution or
melt, and liquid crystalline systems.

ACKNOWLEDGMENTS

We are grateful to P. Schravendijk, A. Arnold, M. De-
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was supported in part by the Volkswagen foundation. One of
the authors (M. P.) acknowledges the support of the Ministry
of Higher Education, Science and Technology of Slovenia
under Grant No. P1-0002.

1624 (2003).


[20] This is achieved by introducing a slab with the width of the effective interaction range, which continues from the transition into the explicit regime, containing hybrid molecules with \( w = 1 \). These hybrid molecules interact among themselves and also with the explicitly resolved molecules as purely all-atom molecules while each of them still has a center-of-mass interaction site for the interactions with the hybrid molecules with \( 0 < w < 1 \) in the interface layer. Since the hybrid molecules with \( w = 1 \) have fully equilibrated rotational and vibrational degrees of freedom and the proper orientation in space, we count the respective slab to the explicit rather than to the transition regime.


