Best Practices for Computing Interfacial Properties from Molecular Simulations

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Supplementary Material

A. Summary of the Force Fields for pure fluids and fluid mixture

A.1 *Coarse Grained Model (CG) for pure fluids*

Fluid	m_{si}	$\varepsilon_{ii}/\kappa_B$ / K	σ_{ii} / Å	λ_{rii}	λ_{aii}
Carbon dioxide (CO_2) [1]	1	353.55	3.741	23.00	6.66
n-decane (*n*-$C_{10}H_{22}$) [2]	3	414.90	4.629	19.61	6.00

Coarse Grained Model (CG) for mixture

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \tag{S.1}$$

$$\varepsilon_{ij} = (1 - k_{ij}) \frac{\sqrt{\sigma_{ii}^3 \sigma_{jj}^3}}{\sigma_{ij}^3} \sqrt{\varepsilon_{ii}\,\varepsilon_{jj}} \tag{S.2}$$

$$\left(\lambda_{k_{ij}} - 3\right) = \sqrt{\left(\lambda_{k_{ii}} - 3\right)\left(\lambda_{k_{jj}} - 3\right)} \quad ; \quad k = a, r \tag{S.3}$$

Mixture	k_{ij}	$\varepsilon_{ij}/\kappa_B$ / K	σ_{ij} / Å	λ_{rij}	λ_{aij}
CO_2 + *n*-$C_{10}H_{22}$ [3]	0.075	348.31	4.185	21.23	6.31

All Atoms for Carbon dioxide (CO_2 : O = C = O) [4]:

$$U(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{r_{ij}} \tag{S.4}$$

$$\begin{aligned} \varepsilon_C/\kappa_B &= 28.129\ K \\ \varepsilon_O/\kappa_B &= 80.507\ K \\ \sigma_C &= 2.757\ \mathring{A} \\ \sigma_O &= 3.033\ \mathring{A} \\ q_C &= 0.6512\ e^- \\ q_O &= -0.3256\ e^- \end{aligned} \tag{S.5}$$

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United Atoms: TraPPE-UA for n-decane (n-$C_{10}H_{22}$: CH_3-8 CH_2-CH_3) [5]

$$U = U^{str}(r) + U^{bend}(\theta) + U^{torsion}(\varphi) + U^{LJ}(r) \quad \text{(S.5)}$$

U^{str} is replaced by a rigid bond between two consecutives UA with a length of 1.54 Å (S.6)

$$U^{bend}(\theta) = \frac{k_\theta}{2}(\theta - \theta_0)^2 \quad ; \quad k_\theta = 62500\ K/rad^2; \theta_0 = 114.0^0 \quad \text{(S.7)}$$

$$U^{torsion}(\varphi) = c_1(1 + cos\varphi) + c_2(1 - cos2\varphi) + c_3(1 + cos3\varphi) \quad \text{(S.8)}$$

$$c_1/\kappa_B = 355.03\ K$$
$$c_2/\kappa_B = -68.19\ K$$
$$c_3/\kappa_B = 791.32\ K$$

$$U^{LJ}(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \quad ; \quad \varepsilon_{ij} = \sqrt{\varepsilon_{ii}\,\varepsilon_{jj}} \quad ; \quad \sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \quad \text{(S.9)}$$

$$\varepsilon_{CH_3}/\kappa_B = 98\ K$$
$$\varepsilon_{CH_2}/\kappa_B = 46\ K$$
$$\sigma_{CH_3} = 3.75\ \mathring{A}$$
$$\sigma_{CH_2} = 3.95\ \mathring{A}$$

Mixture of carbon dioxide (CO_2) + *n*-decane (*n*-$C_{10}H_{22}$)

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\,\varepsilon_{jj}} \quad ; \quad \sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \quad \text{(S.10)}$$

i	***j***	$\varepsilon_{ij}/\kappa_B$ / **K**	σ_{ij} / **Å**
CH_3	CH_2	98.00	3.75
CH_3	CH_2	67.14	3.85
CH_3	C	52.50	1.38
CH_3	O	88.82	2.20
CH_2	CH_2	46.00	3.95
CH_2	C	35.97	3.35
CH_2	O	60.85	2.30
C	C	28.13	2.76
C	O	47.59	1.70
O	O	80.51	0.65

B. Base cases for Molecular Dynamics Simulations using Coarse Grained models included in the text.

In this section, we describe all details to carry out Molecular Dynamics (MD) simulations for three selected cases of Coarse-Grained models: CO_2, *n*-$C_{10}H_{22}$, and CO_2 + *n*-$C_{10}H_{22}$

B.1 *Carbon dioxide: CO_2*

In this case, CO_2 is modelled as a single sphere with the parameters reported in Table A.1. The selected isothermal condition to build the cell is 240 K. According to NIST [6], the vapor-liquid equilibrium (VLE) conditions are:

T / K	***P / MPa***	ρ^L ***/ mol /L***	ρ^V ***/ mol /L***	γ ***/ mN / m***
240	1.2825	24.742	0.75654	11.523

Following the recommendations described in the main text, 3500 sites are selected to describe both VLE and interfacial properties. Therefore, the volume of the simulation cell is:

$$V = \frac{(3500\, molecules)\left(10^{10}\right)^3 \left(\frac{\text{Å}}{m}\right)^3}{\left(\frac{24.742+0.75654}{2}\right)\left(\frac{mol}{L}\right)(N_{av})\left(\frac{molecules}{mol}\right)(1000)\left(\frac{L}{m^3}\right)} = 456022.46\ \text{Å}^3 \qquad \text{(S.11)}$$

Considering that $V = L_x\, L_y\, L_z$, with L_z = (3 to 8) L_x and selected n = 4.442:

$$L_x = L_y = \left(\frac{V}{n}\right)^{1/3} = \left(\frac{456022.46\ \text{Å}^3}{4.442}\right)^{1/3} = 46.824\ \text{Å} \qquad \text{(S.12)}$$

$$L_z = nL_x = 4.442 \times 46.824\ \text{Å} = 208\ \text{Å} \qquad \text{(S.13)}$$

At this stage, it is important to check that $L_x = L_y > 10\ \sigma_{ii}$ (37.41 Å) and $L_z \approx 3$ to 10 L_x. Figure S1 shows a snapshot of this initial configuration.

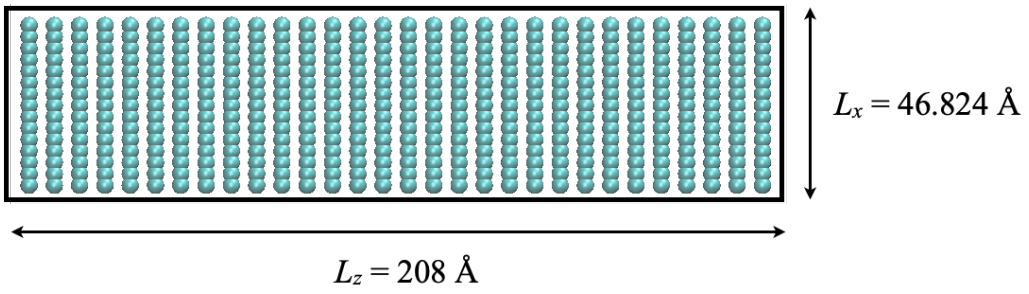

Figure S1. Snapshot of the initial configuration for CO_2 as a single sphere

Following the steps described in the main text, the other important variables needed to carry out MD are summarized in the following table:

Property	*criteria*	*Value*
Cutoff, r_c	$r_c \geq 6\ \sigma_{max}$ and $r_c \leq L_x/2$	$r_c = 6 \times 3.741$ Å $= 22.446$ Å $L_x/\ 2 = 23.412$ Å
del r	$del\ r = 1.5\sigma_{max}$	$del\ r = 5.611$ Å
Thermostat: Nose-Hoover	$\tau_T = 0.5$ to 1 ps	$\tau_T = 1$ ps
Time step (Δt)	Δt ≈ 0.01 to 0.003 ps/step	Δt = 0.003 ps/step

The next step is to run the simulation at high temperature (T_H). Considering that $T_c = 304.128$ K [6] and $T_H >> T_c$, therefore $T_H = 600$ K will be an adequate selection. At this high temperature condition, the MD is running for few steps SS = 50.000 (SS ≈ 50.000 to 100.000). The final configuration at T_H is shown in Figure S2.

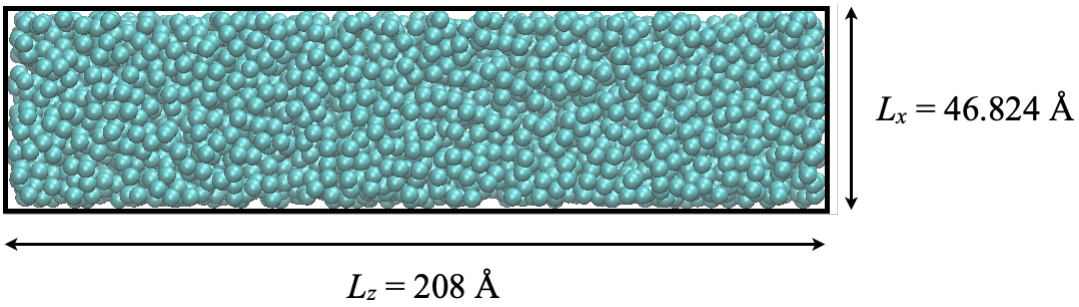

Figure S2. Snapshot of the high temperature configuration for CO_2 represented by a single sphere

Finally, the high temperature configuration (see Fig. S2) is quenched to 240 K, and MD is carried out during the appropriate steps, as it was discussed in the main text and summarized in the following table.

Property	*criteria*	*Value*
Equilibration Steps (ES)	5 to 10×10^6	ES = 5×10^6
Equilibration Time (ET)	10 to 15 ns	ET = 15 ns (ET = ES × Δt)
Production Steps (PS)	PS ≥ 2 × ES	PS = 7×10^6
Production Time (PT)	PT ≥ 2 × ET	PT = 21 ns (PT = PS × Δt)
Total Steps (TS)	TS = ES + PS	TS = 12×10^6
Total Time (TT)	TT = ET + PT	TT = 36 ns

The main final results of this simulation are displayed in Figs. 13, 15-17, and the following table summarizes the final results

source	*T / K*	*P / MPa*	ρ^L */ mol /L*	ρ^V */ mol /L*	*γ / mN / m*
MD - Virial	240	1.4691	25.0298	0.9201	11.059
MD - IK	240	1.3224	25.0298	0.9201	11.150

B.2 *n-Decane: n-$C_{10}H_{22}$*

In this case, n-$C_{10}H_{22}$ is modelled as three tangent spheres with the parameters reported in Table A.1. The selected isothermal condition to build the simulation cell is 350 K. The isothermal vapor-liquid equilibrium (VLE) conditions are: [6]

T / K	*P / MPa*	ρ^L */ mol /L*	ρ^V */ mol /L*	*γ / mN / m*
350	0.003524	4.8206	0.0012178	18.691

Following the same procedure described for CO_2, we selected 5001 sites (1667 molecules) to describe both VLE and interfacial properties. The volume of the simulation cell is:

$$V = \frac{(1667\,molecules)\left(10^{10}\right)^3\left(\frac{\text{Å}}{m}\right)^3}{\left(\frac{4.8206+0.0012178}{2}\right)\left(\frac{mol}{L}\right)(N_{av})\left(\frac{molecules}{mol}\right)(1000)\left(\frac{L}{m^3}\right)} = 1148572.22\ \text{Å}^3 \qquad \text{(S.11)}$$

Considering that $V = L_x\,L_y\,L_z$, with L_z = (3 to 8) L_x and selected n = 6:

$$L_x = L_y = \left(\frac{V}{n}\right)^{1/3} = \left(\frac{1148572.22\ \text{Å}^3}{6}\right)^{1/3} = 57.63\ \text{Å} \qquad \text{(S.12)}$$

$$L_z = nL_x = 6 \times 57.63\ \text{Å} = 345.78\ \text{Å} \qquad \text{(S.13)}$$

where $L_x = L_y > 10\ \sigma_{ii}$ (46.29 Å) and $L_z \approx 3$ to 10 L_x. Figure S3 shows a snapshot of this initial configuration.

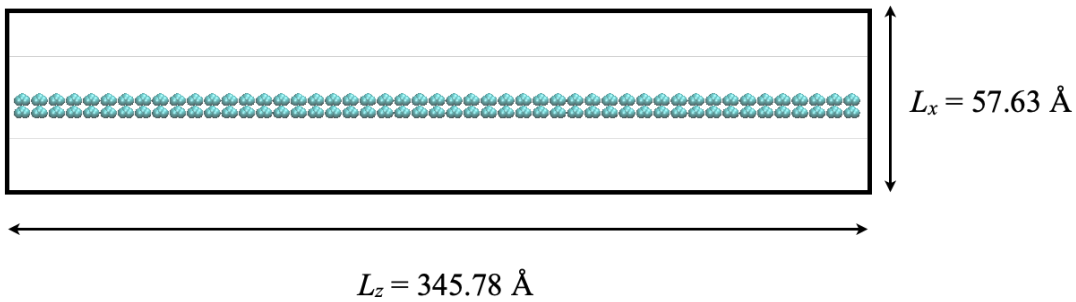

Figure S3. Snapshot of initial configuration for n-$C_{10}H_{22}$ represented by three tangent spheres

Property	*criteria*	*Value*
Cutoff, r_c	$r_c \geq 6\ \sigma_{max}$ and $r_c \leq L_x/2$	$r_c = 6 \times 4$ Å = 27.774 Å $L_x/2$ = 28.815 Å
del r	$del\ r = 1.5\sigma_{max}$	$del\ r$ = 6.943 Å
Thermostat: Nose-Hoover	τ_T = 0.5 to 1 ps	τ_T = 1 ps
Time step (Δt)	Δt ≈ 0.01 to 0.003 ps/step	Δt = 0.003 ps/step

The next step is to run the simulation at high temperature (T_H). Considering that T_c = 617.7 K [6] and $T_H >> T_c$, T_H = 1000 K. At this high temperature, the MD is running for few steps SS = 100.000 (SS ≈ 50.000 to 100.000). The final configuration at T_H is shown in Figure S4.

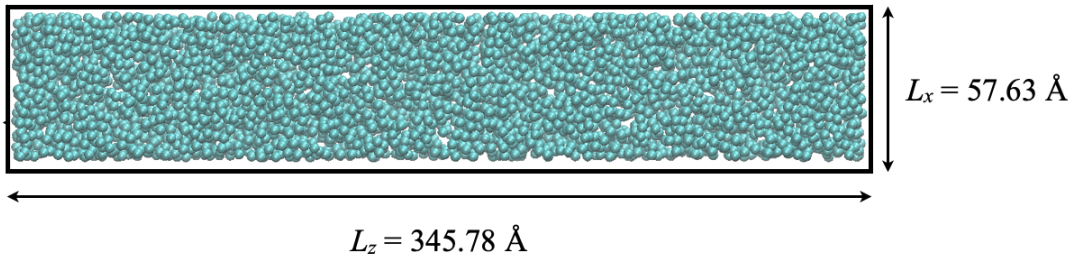

Figure S4. Snapshot of the high temperature configuration for n-$C_{10}H_{22}$ represented by three tangent spheres.

Finally, the high temperature configuration (see Fig. S4) is quenched to 500 K, and MD is carried out using, as it was discussed in the main text**,** the following steps

Property	*criteria*	*Value*
Equilibration Steps (ES)	5 to 10 × 10^6	ES = 5 × 10^6
Equilibration Time (ET)	10 to 15 ns	ET = 15 ns (ET = ES × Δt)
Production Steps (PS)	PS ≥ 2 × ES	PS = 7 × 10^6
Production Time (PT)	PT ≥ 2 × ET	PT = 21 ns (PT = PS × Δt)
Total Steps (TS)	TS = ES + PS	TS = 12 × 10^6
Total Time (TT)	TT = ET + PT	TT = 36 ns

The final results of this simulation are summarized in the following table, which also includes the NIST data [6] and Figure S5 displays the final spatial configuration.

source	*T / K*	*P / MPa*	ρ^L */ mol /L*	ρ^V */ mol /L*	γ */ mN / m*
NIST	500	0.3279	3.8742	0.090	6.637
MD - Virial	500	0.0696	3.8046	0.137	6.335
MD - IK	500	0.3945	3.8046	0.137	6.710

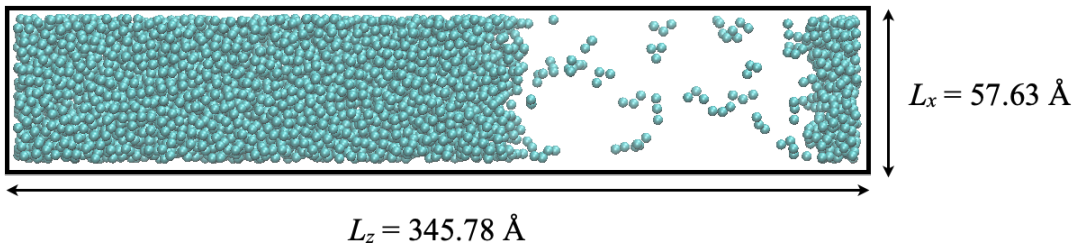

Figure S5. Snapshot of final configuration for n-$C_{10}H_{22}$ represented by three tangent spheres

B.3 *Binary Mixture of Carbon dioxide* (CO_2) + *n-Decane:* (n-$C_{10}H_{22}$)

For this binary mixture, CO_2 is modelled as a single sphere (see Sec. B.1) whereas n-$C_{10}H_{22}$ is modelled as three tangent spheres (see Sec. B.2). From the example 2 described in the main text, the simulation conditions, cell dimension and molecules distribution are summarized in the following table and Figure S6 displays a snapshot of the initial configuration for the mixture.

Property	***Value***
T	344.15 K
$N^L CO_2$	439 sites; 439 molecules
$N^L C_{10}H_{22}$	3711 sites; 1237 molecules
$N^V CO_2$	1817 sites; 1817 molecules
$N^V C_{10}H_{22}$	33 sites; 11 molecules
$N^T CO_2$	2256 sites; 2256 molecules
$N^T C_{10}H_{22}$	3744 sites; 1248 molecules
N^T	6000 sites; 3504 molecules
$L_x = L_y$	76.50 Å
$L_z = 6\ L_x$	459.0 Å

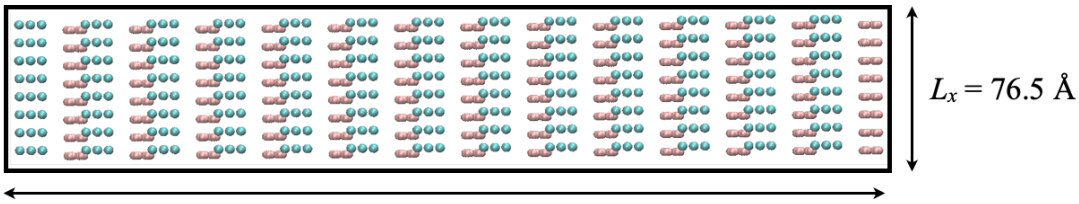

Figure S6 Snapshot of the initial configuration for the mixture CO_2 + n-$C_{10}H_{22}$.
(●) CO_2; (●●●) n-$C_{10}H_{22}$

The other variables to carry out MD are summarized in the following table:

Property	***criteria***	***Value***
Cutoff, r_c	$r_c \geq 6\ \sigma_{max}$ and $r_c \leq L_x/2$	$r_c = 6 \times 4$ Å ≈ 28 Å $L_x/2$ = 38.25 Å
del r	$del\ r = 1.5\sigma_{max}$	$del\ r$ = 7 Å
Thermostat: Nose-Hoover	τ_T = 0.5 to 1 ps	τ_T = 1 ps
Time step (Δt)	Δt ≈ 0.01 to 0.003 ps/step	Δt = 0.003 ps/step

As it was described before, MD is initially run at high temperature (T_H). For the case of mixtures, the critical temperature is a function of the molar fraction and its shape depends on the Type of the mixture. For the case of CO_2 (1) + n-$C_{10}H_{22}$ (2), this mixture is classified as Type II behavior in the van Konynenburg and Scott [7]. According to Juntarachat et al. [8], the experimental values of the critical line are T_c = 607.32 K at x_1 = 0.2051, therefore, T_H = 1000 K. For the other cases, where no experimental information is available, T_H > 1000 K will be an adequate selection. Figure S7 illustrates the final configuration at T_H after 100.000 steps.

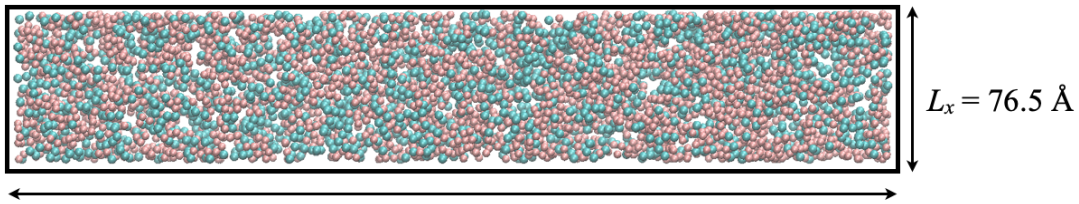

Figure S7 Snapshot of the high temperature configuration for the mixture CO2 + n-$C_{10}H_{22}$
(●) CO_2; (●●●) n-$C_{10}H_{22}$

Following the same procedure described before, the high temperature configuration (see Fig. S7) is quenched to 344.15 K, and MD is carried out using the following steps, as it was discussed in the main text.

Property	*criteria*	*Value*
Equilibration Steps (ES)	20 to 30 × 10^6	ES = 25 × 10^6
Equilibration Time (ET)	70 to 80 ns	ET = 75 ns
		(ET = ES × Δt)
Production Steps (PS)	PS ≥ 2 × ES	PS = 50 × 10^6
Production Time (PT)	PT ≥ 2 × ET	PT = 150 ns
		(PT = PS × Δt)
Total Steps (TS)	TS = ES + PS	TS = 75 × 10^6
Total Time (TT)	TT = ET + PT	TT = 225 ns

The final results of this simulation are summarized in the following table and Figure S8 displays the final spatial configuration. For further information relates to this mixture and its MD results, the reader is redirected to Ref. [3]

source	*P / MPa*	x_1	y_1	ρ^L / mol /L	ρ^V / mol /L	γ / mN / m
Exp.[3]	3.000			51.011	697.114	14.23
	3.587			62.555	698.983	13.46
MD - Virial	3.197	0.3289	0.9928	59.918	701.183	14.64
MD - IK	3.386	0.3289	0.9928	59.918	701.183	13.99

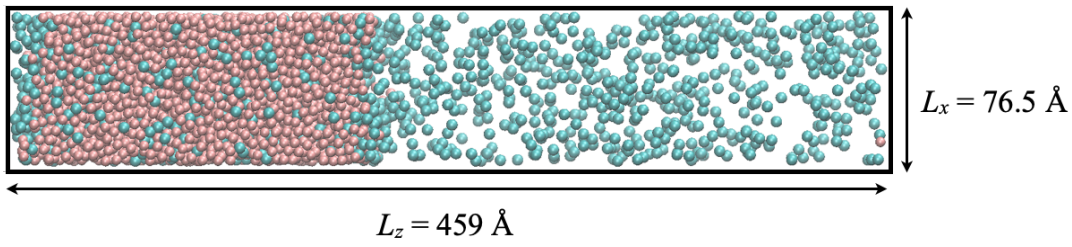

Figure S8 Snapshot of final configuration for the mixture CO_2 + n-$C_{10}H_{22}$.
(●) CO_2; (●●●) n-$C_{10}H_{22}$

C. Basic subroutine to compute densities, normal and tangential pressure in DLPOLY

```
#include<fstream>
#include<iostream>

using namespace std;

int main() {
  const int bins=250;
  const double kB=0.831451115; // Boltzmann constant in internal units
  double dens[bins],xstress[bins],ystress[bins],zstress[bins];
  double ddum,Lx,Ly,Lz,temp;
  int dum;
  char line[256],word[12];

  ifstream prof,config;
  ofstream out;

  config.open("CONFIG");

  config.getline(line,256);

  config >> dum;   config >> dum;   config >> dum;
  config >> ddum;

  config >> Lx;   config >> ddum;   config >> ddum;
  config >> ddum; config >> Ly;     config >> ddum;
  config >> ddum; config >> ddum;   config >> Lz;

  config.close();

  //  cout << Lx << " " << Ly << " " << Lz << endl;

  // This requires the temperature be at the 3rd line of CONTROL!

  config.open("CONTROL");

  config.getline(line,256);
  config.getline(line,256);
  config >> word;
  config >> temp;
  config.close();

  cout << temp << endl;

  prof.open("PROFILES");
  out.open("profiles.dat");

  for(int i=0;i<bins;i++) {
```

```
    dens[i]=0;
    xstress[i]=ystress[i]=zstress[i]=0;
  }

  int iter=0;

  while(prof >> dum) {
    iter++;
    cout << "Step " << dum << " ,iter " << iter << endl;
    for(int i=0;i<bins;i++) {
      double value;
      prof >> value;
      dens[i]+=value;
      prof >> value;
      xstress[i]+=value;
      prof >> value;
      ystress[i]+=value;
      prof >> value;
      zstress[i]+=value;
    }
  }

  double den=((double)iter)*Lx*Ly*Lz/((double)bins);

  for(int i=0;i<bins;i++) {
    double x=i*Lz/((double)bins);
    out << x
      << " " <<    dens[i]/den
      // 2 from original overcounting of stress
      << " " << xstress[i]/den/(2*kB*temp)
      << " " << ystress[i]/den/(2*kB*temp)
      << " " << zstress[i]/den/(2*kB*temp)
      << " " <<(zstress[i]-(xstress[i]+ystress[i])/2.0)/den/(2*kB*temp)
      << endl;
  }

  prof.close();
  out.close();
  return 0;
}
```

D. Folders for examples

In the supplementary files, we are included the input files to carry out MD under three suites: DLPOLY [9] (../input/DLPOLY/), LAMMPS [10] (../input/LAMMPS/) and HooMD-blue [11] (.../input/HOOMD/)

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[11] hoomd-blue , http://glotzerlab.engin.umich.edu/hoomd-blue/ (last visit 15/04/2020)