Further validation of pathwise SA on CH_4

Various observable plots - $g(r)$

We have included some figures in this section for the sake of completeness. Reference to these results is indirect through tables of the main text in the Results section of the CH_4 model.

The $g(r)$ graph for the positively perturbed ϵ_{LJ} directions are above the unperturbed graph in Figure 1 which is justified from the increased depth of the potential well.

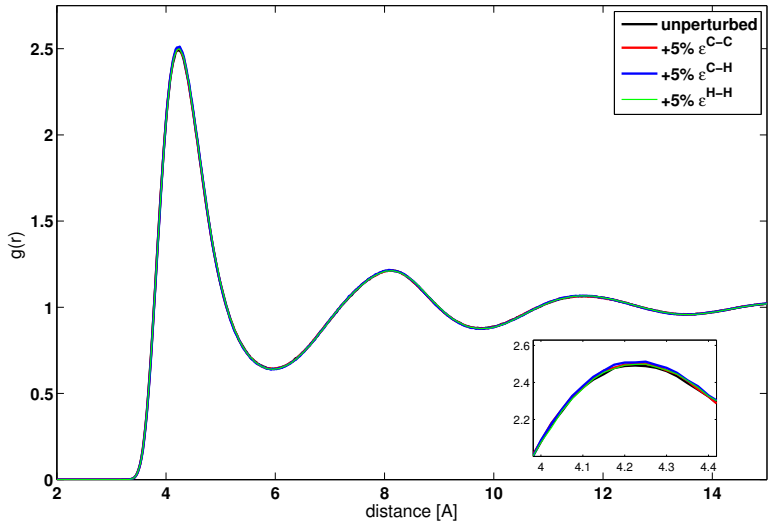

Figure 1: CH_4 molecular $g(r)$ for +5% perturbations on ϵ_{LJ}. The tail of the plot varies slightly hence the zoomed region differs more. As in the LJ fluid case, ϵ_{LJ} affects the height of the first peak.

Figure 2 shows that the most sensitive parameter r_0 the RE methods predicted, doesn't have the leading role with respect to the molecular structure, as the latter is quantified through $g(r)$. From a physical point of view the liquid CH_4 can settle in a similar configurational bulk state after elongating the bonds. Note that as discussed above, the Pinsker inequality provides an upper bound only; thus the example discussed here illustrates this limitation. Plots for perturbations on the bond length and angle constants and θ_0 did not vary much as the rest of the observables (see Figure 3).

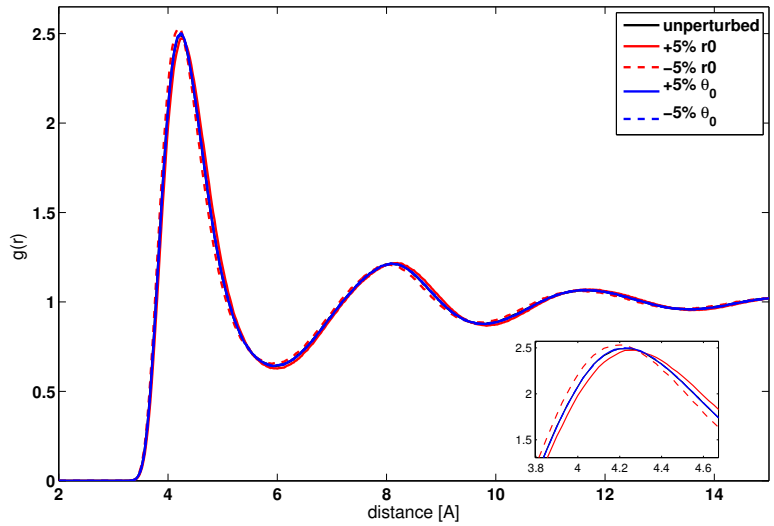

Figure 2: CH_4 molecular $g(r)$ for $\pm 5\%$ perturbations on r_0 andθ_0. The bond length parameter is an order of magnitude more sensitive than the angle parameter w.r.t. the L_2 norm (see Table).

FIM matrix

A representation of the FIM matrix for the CH_4 model is shown in Figure 4. We can clearly see the interconnection-correlations of the parameter sensitivities as we do not only rely on the diagonal elements. Further eigenvalue analysis can provide information on the most sensitive directions as well.

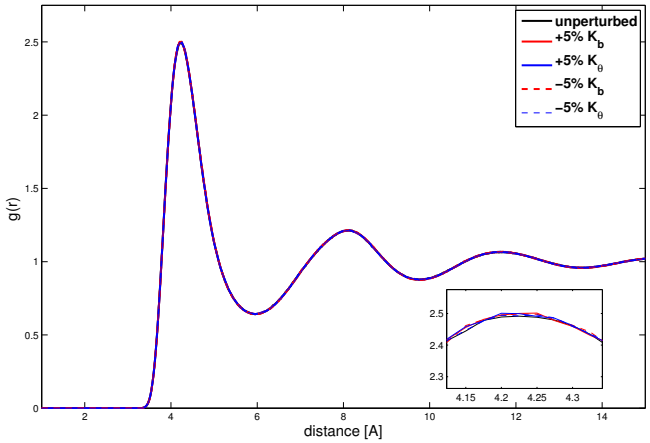

Figure 3: CH_4 $g(r)$ for $\pm 5\%$ perturbations in constants.

Additional observables

Another way to get better insight in the effect of parameter sensitivities is by monitoring another observable. We aimed in the construction of bond and angle distributions upon perturbation of each parameter separately. Figures 6 and 5 summarize our results for a $+5\%$ perturbation. We expect that these intra-molecular observables are more sensitive to the intra-molecular parameters.

Here r_0 plays and important role to the bond length r as the distribution mean is moved to the right and the variance has increased. In Figure 5 the difference between the expected value of the perturbed and unperturbed stands out and Pinsker inequality suggests that we expect RER increase towards this direction, which is validated in Figure 8.

Furthermore r_0 affects the distribution of the angle θ by increasing the variance as well. Following this, the constants K_b, K_θ act on the shape of the corresponding r, θ distributions which is expected via the functional form of V_{bond} and V_{angle}. CH_4 is a symmetric molecule so the θ range cannot vary outside a range defined by the model. Even a larger K_θ angle cannot alter the angle distribution as the K_{bond} constant does to the bond distribution in Figure 5. On the contrary, an increase in the bond length restricts the angle range and more mass is concentrated towards the mean of the angle distribution. No significant deductions can be made from the remaining plots.

We conclude here that parameter sensitivities differ from one observable quantity to another and it is in the nature of the system under examination which ones the modeler chooses. Our proposed methodology focuses on the

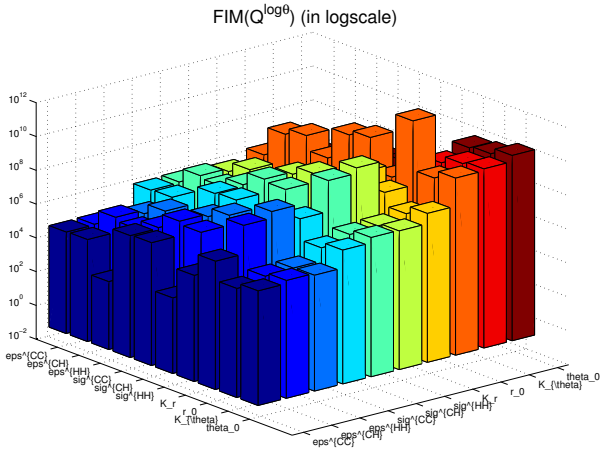

Figure 4: FIM matrix where the gradient is wrt $\log(\theta)$ (in logscale).

distance between probability trajectories and no a priori conclusions can be made for the expected value of an observable on these trajectories.

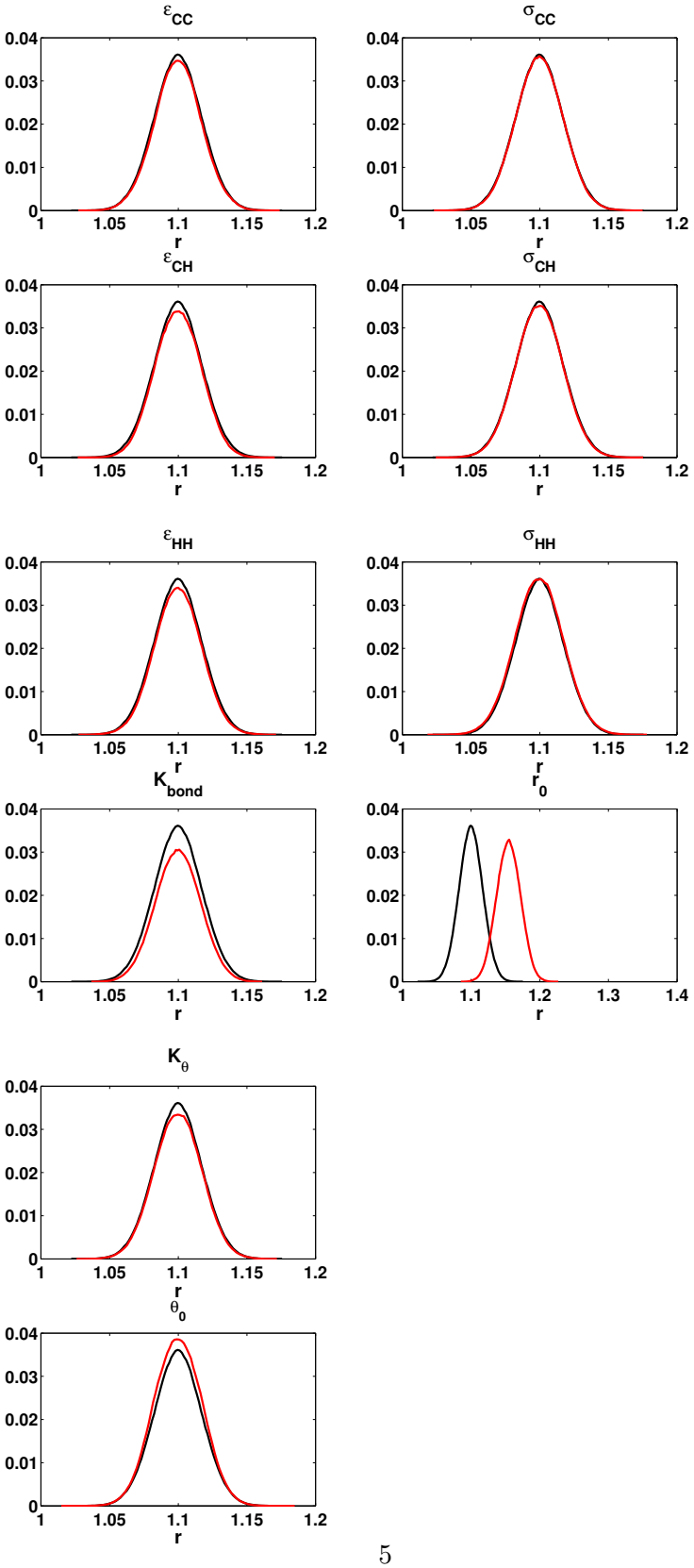

Figure 5: CH_4 bond r distributions for different perturbation directions by +5%. Colored lines indicate pertrurbed distributions. RE computations indicated r_0 as the most sensitive parameter and it is validated for this observable quantity.

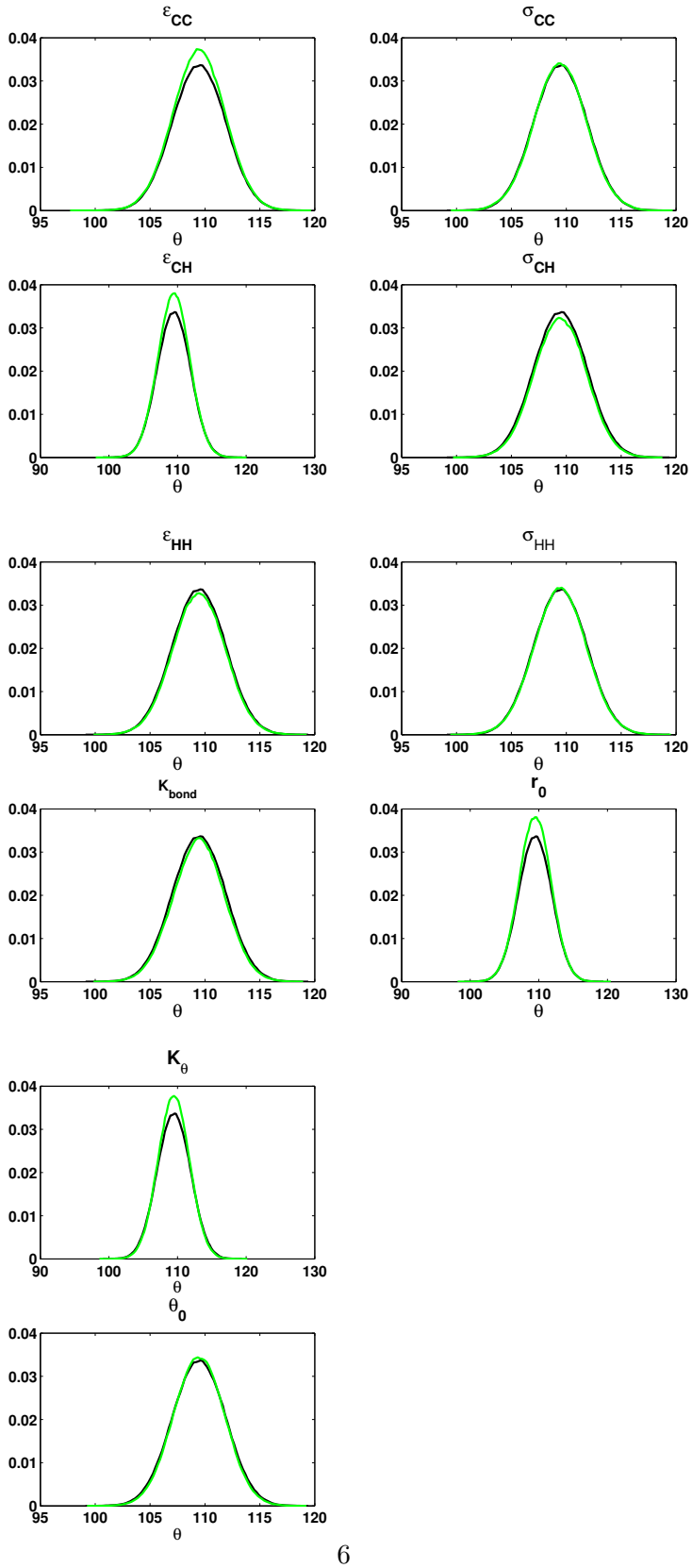

Figure 6: CH_4 angle θ distributions for different perturbation directions by +5%. Colored lines indicate pertrurbed distributions and the horizontal axis is in degrees. The symmetric topology for the CH_4 molecule does not allow the angles to oscillate in another angle range when K_θ is perturbed (last plot).

Simulation parameters

The simulation parameters for both systems are summarized in Table 1. Although we utilized our own MD code for the simulations, our results are reproducible with other MD packages (LAMMPS, Gromacs, etc.) as well.

parameter	LJ fluid	CH_4
steps per RER calculation	40	40
steps per FIM calculation	40	40
steps for equilibration	10^4	10^5
simulation steps	10^5	10^6
steps for observables	10^5	10^5
bin length in $g(r)$	$0.025\sigma_{LJ}$	$0.025\mathring{A}$
multiple origin steps in MSD	5	100
samples in block averaging (P)	100	50
r_{cut} value	$4\sigma_{LJ}$	$15[\mathring{A}]$ $(= 5\sigma_{LJ})$
Δt	10^{-3}	0.5 fs

Table 1: simulation run parameters