Reviewer’s comments

Rich’s comments

Our response

Note: Blue sentences that start with “!” are comments that will be deleted eventually.

**Response to Reviewer #2**

**1. Introduction**

1.1 A fair account of earlier work on integration methods should mention that various integration methods have allowed to extend VLE simulations much below the normal boiling point (references 8, 10, 52, 60, 62). The answer appears insufficient.

[8] M. G. Ahunbay, S. Kranias, V. Lachet, P. Ungerer, Prediction of thermo-dynamic properties of heavy hydrocarbons by Monte Carlo simulation,Fluid Phase Equilibria 224 (1) (2004) 73–81. doi:10.1016/j.fluid.2004.06.053.

[10] C. Vega, E. Sanz, J. L. F. Abascal, E. G. Noya, Determination of phase diagrams via computer simulation: Methodology and applications to water, electrolytes and proteins 20 (2008). arXiv:0901.1823, doi:10.1088/0953-8984/20/15/153101.

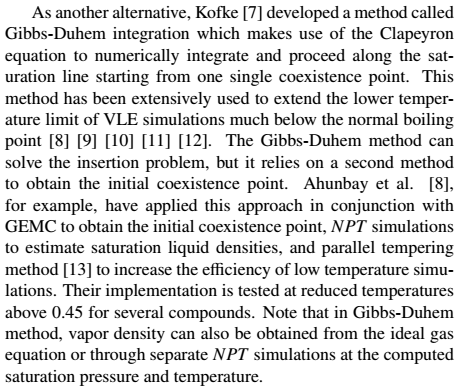
[52] P. Ungerer, C. Beauvais, J. Delhommelle, A. Boutin, B. Rousseau, A. H. Fuchs, Optimization of the anisotropic united atoms intermolecular potential for n-alkanes, Journal of Chemical Physics 112 (12) (2000) 5499-5510. doi:10.1063/1.481116.

[60] C. Vega, J. L. Abascal, I. Nezbeda, Vapor-liquid equilibria from the triple point up to the critical point for the new generation of TIP4P-like models: TIP4P/Ew, TIP4P/2005, and TIP4P/ice, Journal of Chemical Physics 125 (3). doi:10.1063/1.2215612.

[62] M. Yiannourakou, P. Ungerer, V. Lachet, B. Rousseau, J.-M. Teuler, United atom forcefield for vapor-liquid equilibrium (VLE) properties of cyclic and polycyclic compounds from Monte Carlo simulations, Fluid Phase Equilibriadoi:10.1016/j.fluid.2018.07.001.

We added a sentence to the following paragraph in the Introduction section in order to acknowledge the above-mentioned works (now references 8-12) that used Kofke’s Gibbs-Duhem integration method:

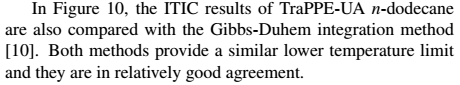
! Please see my comment to revise this sentence to read, “limit of coexistence calculations…” because we have not yet defined “VLE.”



1.2 Coexistence properties from Gibbs Duhem integration : OK with the answer

1.3 Comparison with earlier VLE prediction on n-dodecane : the revised version is changed but it does not comment the similar performance of GDI and ITIC in terms of accessible temperature range for this compound. The answer is acceptable but can be improved.

In response to the reviewer’s comment, the following paragraph was added to Section 7:

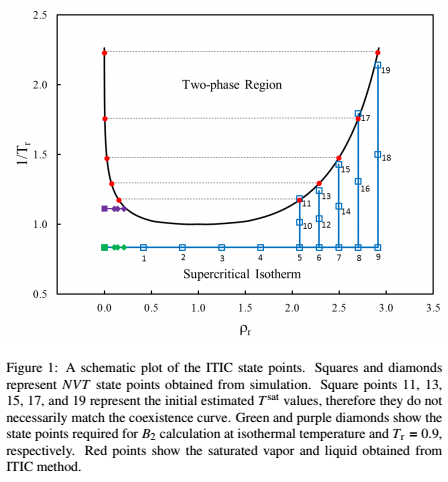


**2. Theory**

2.1 Figure 1 does not show the case when saturation temperature is unknown. The revised version is indicating that the Figure 1 relates to the specific case of known saturation temperature (or accurate estimate). Adding the case of a “rare aromatic molecule” (i.e. 1-napthalenyl, 4 phenanthrenyl butane) is fine, but the initialization has benefited from earlier GEMC results from ref 62. Neither precise values of Tsat estimated nor result tables are provided for this compound. The answer is acceptable but can be improved.

[62] M. Yiannourakou, P. Ungerer, V. Lachet, B. Rousseau, J.-M. Teuler, United atom forcefield for vapor-liquid equilibrium (VLE) properties of cyclic and polycyclic compounds from Monte Carlo simulations, Fluid Phase Equilibriadoi:10.1016/j.fluid.2018.07.001.

Figure 1 was modified to clearly show that the Tsat values are not known a priori, therefore the square points 11, 13, 15, 17, and 19 do not match the coexistence curve. Instead, these points are arbitrarily placed above or below the coexistence curve.

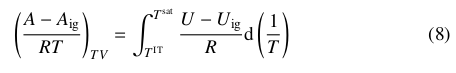
I don’t really like the arbitrary placement above and below. I like how we had them before (all below) because I think it is more common for someone to make a uniform initial estimate that are all too low. I do think including the red points is helpful though.

I also think we could also help address the “unknown Tsat” scenario by modifying Figure 2 slightly. Should we have an outer loop that shows that if the final Tsat deviates strongly from the Tsat\_est, we can perform additional simulations. We could include this at the very end of the figure or after the “Calculate Tsat\_new from Z vs 1/T” line by including a junction “\delta Tsat < tol?” (or \delta 1/Tsat < tol) (maybe a different tol variable) where if yes you continue as normal but if no you loop back to the first step for improved Tsat\_est.

We would like to emphasize that no data from Ref. [62] were used to initialize Tsat values. Initial saturation temperatures were estimated using simple linear regression shown in Figure 12 (a). The GEMC results included in Figure 12(b) and 12(c) were obtained from new GEMC simulations that we performed independent of the ITIC analysis. We have clarified in the text and the figure caption that these GEMC data are not literature values.

We thank the reviewer for reminding us about the missing tables. Tables of NVT simulation results, GEMC results, and ITIC results are now included in Supplementary Material.

2.2 Ambiguity of equation 8 .

Using the same notations Adep(T,V) = (A(T,V)-AIG(T,V))/RT and Udep(T,V) = (U(T,V)-UIG(T,V))/RT as in the manuscript, equation (8) should be written :



The authors seem to confuse the dummy variable *T* with the end points (𝑇𝐼𝐶,𝑇𝑠𝑎𝑡) of the interval over which integration proceeds. The ambiguity may explain the error in equation (17) mentioned in point 2.3 below. The answer is clearly insufficient.

We apologize for misunderstanding the reviewer’s comment in the previous review letter. Equation 8 specified above is indeed ambiguous. In the light of the reviewers’ comments we have reformulated the entire Section 2.1 and 2.2. The equation that replaced the Equation 8 mentioned above is



This equation is used to calculate the change in Helmholtz energy along an isochore. From a reference state to a state of interest.

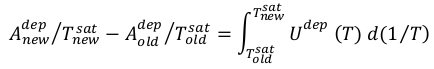
The Eq. (8, corrected) mentioned above, however, does not seem to quite agree with our understanding, because the integrand is lacking a T factor, i.e. it should be TUdep instead of Udep. Consequently, the Adep terms on the LHS are not divided by temperature. We admit that our less conventional way of defining departure function(e.g. (A-Aig)/RT instead of A-Aig ) might have caused this confusion. In our opinion, the following would be correct according to the notation used in our work

Or

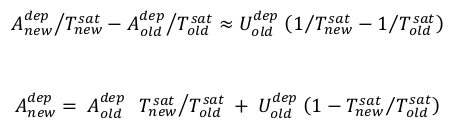
2.3 Uncorrected error in equation (17)

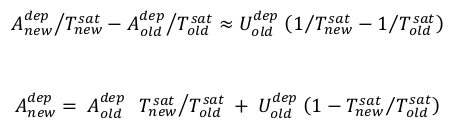
The constant volume V will be dropped for simplicity in the next equations of this review:

The true mathematical integration of equation (8, corrected) at constant volume yields :



For small variations of *Tsat* we may consider as a first order approximation that the derivative as constant, thus we get :

Or



Comparing with equation (17) of the original text (unchanged in the revised version), it seems that the authors have omitted the factor 𝑇𝑛𝑒𝑤𝑠𝑎𝑡/𝑇𝑜𝑙𝑑𝑠𝑎𝑡 of 𝐴𝑜𝑙𝑑𝑑𝑒𝑝 in the right hand side of this equation. This is a serious flaw that may explains that the convergence of the ITIC method as presented in this article is decreasing when initializing Tsat far away (Figure 8).

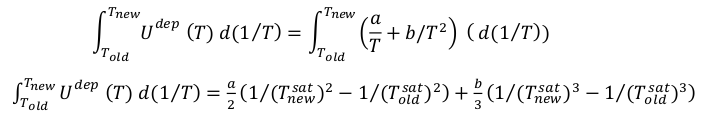
In explaining how they obtained equation (17) the authors refer to the linear dependence of *TUdep* as varying linearly with *1/T*.. They do not discuss specifically this point in the main text, but let us take it for granted, as it may be a better approximation than considering *Ude*p constant. The linear dependence of *TUdep* vs *1/T* implies that there are two constants a and b such that :

*TUdep= a + b/T*

or equivalently

*Udep=a/T + b/T2*

Then, using the equation (8,corrected) we get through exact integration :



This expression does not match the proposed equation (17), and the problem of having dropped the factor 𝑇𝑛𝑒𝑤𝑠𝑎𝑡/𝑇𝑜𝑙𝑑𝑠𝑎𝑡 of 𝐴𝑜𝑙𝑑𝑑𝑒𝑝 remains unsolved. It is likely that the confusion between dummy variables and interval end points in equation (8) has caused some errors in deriving equation (17) in the initial ITIC method. The answer of the authors (no changes except a short additional sentence in text) appears insufficient.

Assuming that the reviewer’s concern about ambiguity of Eq.(8) is resolved and our understanding of Eq.(8, corrected) is valid, we believe that Eq.(17) will no longer be incorrect. The factor 𝑇𝑛𝑒𝑤𝑠𝑎𝑡/𝑇𝑜𝑙𝑑𝑠𝑎𝑡 of 𝐴𝑜𝑙𝑑𝑑𝑒𝑝 in the above derivation originated from dividing the Anewdep and Aolddep by their corresponding temperatures. Also, omitting the T factor in the integrand causes the second derivation above to be incorrect.

2.4 (blank item, the referee apologizes for this numbering error in previous report)

2.5 Correlation of saturation pressure and acentric factor : the revised version makes use of Antoine’s law to correlate vapor pressure (equation 27) , and it does no more refer to Lee Kesler’s method to evaluate the acentric factor. This improves the consistency of the ITIC method. The answer is OK.

**3. ITIC validation**

3.1 provide initial estimates used for Tsat for dodecane in Tables : OK with the answer

3.2 Sensitivity of VLE results to the virial coefficients : I understand from the reply and added text that the sensitivity to virial coefficients is low. The answer appears OK

3.3 Show the influence of initializing Tsat far away from the final solution : the graph showing the successive iterations for dodecane in Supplementary material in a modified figure 3b is OK. Good point. Answer is OK.

3.4 In Figure 6, how is it possible that round Tsat values are imposed ? The proposed modification of figure 6 with added explanation appears reasonable. Answer is OK

3.5 In Figure 7 the final Psat obtained by ITIC depends on the initialization. It is OK that the errors are low, but if the iterative method is well designed the deviations should not increase when initializing far away from the final solution. The example selected here, n-dodecane, is a well-known compound for which REFPROP is reliable, but small convergence issues might have larger impact on more complex molecules. Answer is acceptable, but can be improved.

It is true that small convergence issues might introduce large impacts for complex molecules, but we believe that the increased deviations when Tsatest is initialized far away from the final solution is inevitable. We emphasize that the iterations do not involve running new simulations, therefore the Z and U values at Tsatnew do not improve with each iteration. If additional simulations were performed at Tsatnew, the final Psat value would not depend on the initial Tsatest.

3.6 Accuracy limited to 0.1% : mentioned in section 2.3. OK with the answer.

**4. Simulation details**

4.1 It is surprising to read that “the MC method with fixed bond lengths is favored due to lower fluctuations at low density”. In the revised manuscript “fluctuations” is replaced by “uncertainties” which is more correct. However this is applies also to MC with variable bond lengths, as the TraPPE-UA extension of reference 62. Answer acceptable, but can be improved.

We agree that MC with flexible-bond also involves less uncertainties. Since the “fixed-bond” in the above-mentioned sentence mostly refers to MD, we removed it from that sentence.

4.2 is it possible to apply the ITIC method at imposed Tsat = 0.65, 0.75 and 0.85 in reduced units ? The sentence has been reformulated. Answer is OK.

! In my version that sentence does include “approximately”. Maybe you were looking at an old version of the manuscript? Good, it is in my current version.

4.3 …computation time required by successive iterations on saturation temperature in ITIC. Explanation provided in section 2.3 of the revised version. Answer is OK.

4.4 misleading statement “for reduced temperatures of 0.45 and 0.55 … GEMC is not feasible for n-dodecane” . The revised version includes a statement that GEMC + GDI is also able to provide low temperature VLE data. However this referee maintains that it would be fair to compare ITIC, which is basically an integration method, with other state-of the art integration methods. Among the references cited by the authors, there are at least five articles applying integration methods to VLE properties or to forcefield parametrization at low reduced temperatures (references 8, 10, 52, 60, 62). Answer is acceptable, but can be improved.

Although the reviewer is letting this pass, are we satisfied? Do we need to do a better job representing the literature integration methods and how they have been applied?

! I’ve been thinking about digging into Gibbs-Duhem literature to compare ITIC at low T range with Gibbs-Duhem results. But I think that requires running simulations as it is not likely to find GD results for systems that we already simulated. Let’s discuss this further!

I think the reviewer still wants us to compare both the temperature range and the computational cost of ITIC with GEMC+GDI. I don’t know if we want to open up that can of worms. I think we have made enough changes (especially if we include the ITIC at 0.3 for ethane) to show the value of ITIC.

4.5 Initialization of NVT simulations of the liquid phase . The revised version is pointing to Packmol when GOMC or LAMMPS is used and to Cassandra and GROMACS internal initialization features. This referee regrets that no detail is given on these features (e.g. how to avoid internetted cycles, applicability at low reduced temperature). Answer is acceptable, but can be improved.

! Should we write something here as a response? I don’t think so

I do not think we need to worry about all these details. Basically, if you can build the box you can run ITIC. There are lots of well-known tricks for building boxes at high densities for complex structures, we do not need to reinvent the wheel here.

**5 Calculation of virial coefficients**

**6. Finite size effects**

6.1 Figure 9 , divergence of the pressure determination in the zero density limit when the molecule has internal degrees of freedom. The revised version explains that in MD, intermolecular collisions may not be sufficiently frequent to equilibrate all degrees of freedom, and provides an additional figure in Supplementary material. Section title is changed, which is a good point. Answer is OK.

I think we should actually make Section 6 a subsection for Section 5, i.e., change Section 6 to Section 5.1 (or 5.2 if we change what is currently in Section 5 into Section 5.1). The reason being that both Sections 5 and 6 are about calculating virial coefficients. Section 5 focuses on the approach and derivation, while Section 6 focuses on obtaining good simulation results at low densities in order to obtain good virials.

! I totally agree with you, but that will affect a lot of references in the review letters. maybe consider this the last thing to do before final submission?

You make a fair point. However, I would argue that only Sections 7 and 8 would be affected by the renumbering, and I don’t think the reviewer is going to be confused since Results and Conclusions are pretty clear. But we can certainly wait until after the review process is done (if we don’t forget). For now, could you just create the subsection line in the latex file and comment it out? Then we can just uncomment it when the time comes.

6.2 Finite size effects on the compressibility factor Z and on the internal energy U for dense (liquid) phases. The revised version mentions finite size effects for ethane and acknowledges the need for further investigation. Answer is OK.

**7. Example simulations**

7.1 Figures 10 and 11 : mention Tsat initialization of ITIC for methane, ethane, isobutane , isohexane, dodecane and TIP4P/2005 examples. The revised version indicates that initialization is performed with DIPPR data (reference 46). Answer is OK.

7.2 Figure 11 : compare with dodecane results GEMC + TI using TraPPE-UA [ Ungerer et al. , JCP, 112, (2000), 5499] . In the revised version these results are added in Figure 11. Answer is OK.

**8. Conclusions**

8.1 application range of GEMC + TI versus ITIC methods in terms of reduced temperatures. In the revised version the computational load of ITIC is compared to GEMC or with GEMC + TI, which is fine. However the question raised by this referee in pint 8.1 was rather about the application range : is ITIC able to predict VLE down to Tr=0.3, as required for applications ? This point should be addressed in the conclusion. Answer is acceptable, but can be improved.

To finally put this whole Tr=0.3 thing to bed, can we just apply ITIC to a compound where the triple point is around 0.3? For example, ethane has a reduced triple point temperature of 0.296. Of course, we might run into the challenge that the triple point for the force field is considerably higher than the triple point for the real compound, such that we are in the solid phase at these low temperatures.

Is there a simpler way to prove that we can use ITIC at 0.3? For example, by using the REFPROP data instead of simulations. Unfortunately, the example compound for REFPROP (n-dodecane) has a reduced triple point temperature of 0.4, so it is not a satisfactory candidate. But would it be sufficient to analyze ethane using REFPROP data?

I think that simulating TraPPE-C2 near the triple point (90 K) would satisfy the reviewer. We would then need include this in Figures 10 and 11 and also point it out in the results discussion.

! Todo: Run TraPPE-C2 simulations with Trmin=0.3

8.2 The authors may insist on ITIC advantage = it avoids the implementation of transfer moves in GEMC or GCMC. The revised text refers to the low acceptance of these moves. Answer is OK.

**Response to Reviewer #3**

The authors have made revisions to address some of the concerns raised in my first review, but several of the issues remain unresolved and my second look through the manuscript has revealed  
additional issues that need to be fixed before publishing.  
  
**Comment #6**  
Please also note that the derivation seems to switch back and forth between k\_B (Boltzmann's contant, please include subscript B) in eq. 4, 5, 6 and 7 and R in eq. 2, 3, 8 and following.  Please choose one or the other.

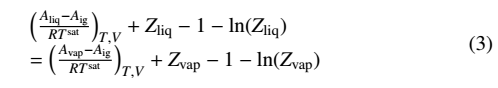
The RHS of equation 8 is now a definite integral (great), but it's still wrong because the temperature of the LHS is not indicated.  In fact, the LHS is a difference in free energy between T^sat and T^IT.

  
Even with the "single molecule" handling of the ideal gas energy, I'm still concerned that the derivation is incorrect.  The errors are masked by the confusing approach taken and sloppiness like the LHS of eq. 8.  This is repeated in Eq. 10 and 12.  Eq. 10 does not yield beta(A\_liq-A\_ig), but rather  
  
beta Aex(rho\_liq,T^sat) - beta Aex(rho=0,T^IT))  
  
Eq. 12 does not yield beta(A\_vap-A\_ig), but rather  
  
beta Aex(rho\_vap,T^sat) - beta Aex(rho=0,T^sat))  
  
Given that the reference free energies are for different temperatures, they will not cancel when substituted into eq. 3.

Please do a proper derivation.  The derivation would be simpler (and less confusing and prone to error) if absolute free energies are obtained and used in eq. 1.  I suspect that in the end, no measurement of ideal gas potential energy will be needed.  
  
If the ideal gas potential energy is still needed, then complexity of the single molecule method seems to be overstated.  First, the authors do not state what is so bad about using Nose-Hoover for a single-molecule simulation.  Second, most molecular dynamics implement thermostats beyond Nose-Hoover (is a Nose-Hoover chains thermostat sufficient?).  The Langevin thermostat is a common choice and is specifically implemented in LAMMPS.

We thank the reviewer for pointing out the issue of switching between k\_B and R. We decided to always use R. We agree with the reviewer that Equation 8 as written above is wrong and ambiguous. The RHS of the equation is indeed the difference between Adepsat and AdepIT. The correct form of this equation would be

Hence, derivations in Section 2.1 and 2.2 were reformulated by defining a reference state, i.e ideal gas at Tsat. The goal is to find a representation for all terms in Eq (3)

Both Aliqdep and Avapdep in the above equation are defined with respect to ideal gas state at saturation temperature. Using a similar notation used by the reviewer in the previous report, the path from saturated liquid and vapor to ideal gas at Tsat are illustrated as follows.

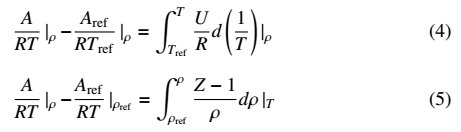
On the vapor side the ideal gas at Tsat is connected to saturated vapor through one isotherm:

(0,Tsat) =====> (ρV,Tsat)

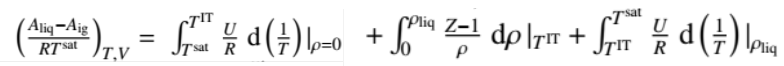
On the liquid side the ideal gas at Tsat is connected to saturated liquid though an isochore, an isotherm, and another isochore:

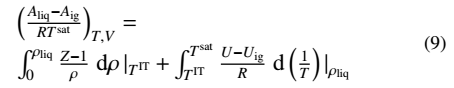
(0,Tsat) ==1==> (0,TIT) ==2==> (ρL,TIT) ==3==> (ρL,Tsat)

Per reviewer’s suggestion, we are now incorporating absolute Helmholtz energies into the derivation in order to clarify the derivation and avoid errors. The following two equations are general formula used to calculate the change in Helmholtz energy during an isochoric and isothermal path, respectively:

Using virial expansion truncated at B3term and Eq (5), we obtain the following equation for Avapdep

Aliqdep is obtained by using Eq (4) and (5) along the isochores and the isotherm

Since the first integral is evaluated at zero density the integrand is actually Uig/R, therefore Aliqdep can be rewritten as

Now Eq. (7) and (9) are substituted in Eq. (3) to obtain vapor density. The result of the reformulated derivation is identical to the previous derivation and the ideal gas potential energy is still needed.

Regarding the single molecule simulations, the reviewer raises a good point that Nose-Hoover chains thermostat are typically sufficient in practice, although in theory this would require an infinite chain of thermostats. We refer to the literature for a detailed explanation of why a single bath is inadequate, but essentially this is an issue of ergodicity. Also, note that “stochastic dynamics” is sometimes referred to as (velocity) Langevin dynamics. Our intent was simply to provide a word of caution when running single molecule calculations. We have modified the manuscript and the supporting information as shown below:

! I could not compile the PDF to copy the needed section  
**Comment #7**  
Concerning solving eq. 14, I don't see how you can solve eq. 14 by itself because it has more than one unknown -- vapor density and Tsat (which determine Zliq, B2 and B3).  These are handled by using 14-17, but as it is described in section 2.2, eq 14 (and 15) can be solved directly.

! Need to find a proper way to respond to this comment

As our new derivation in Section 2.1 has modified the numbering of equations, we note that the authors comment regarding Equations 14-17 now pertains to Equations 11-14. We will utilize the updated numbering notation in our response.

Figure 2, which is a step-by-step explanation of the algorithm, is helpful when responding to the reviewer’s question. The step “Calculate rhovap (Eq. 11), Psat (Eq. 12)” is performed following the step “Calculate Tsat\_new…” Therefore, Tsat is assumed to be a known quantity when solving Eq. 11, such that rhovap is the only unknown. Once rhovap and Psat are computed, the next steps are to “Update Zliq (Eq. 13)” and “Calculate Tsat\_new.” Thus, Zliq is also assumed to be constant when solving Eq. 11.

Setting Zliq and rhovap to an initial near-zero value does not pertain to solving Eq 11, this refers to the overall iteration process. As mentioned above, Zliq is updated with each iteration. An initial near-zero Zliq value is used to estimate the first iteration of Tsat\_new. The initial near-zero value of rhovap is used when solving Eq 11 for the first overall iteration. However, subsequent iterations solve Eq 11 using the previous iteration values for rhovap.

Because the iterative ITIC algorithm is not described until Section 2.3, we have modified Section 2.2. to clarify that Equations 11 and 12 can only be solved for a given value of Tsat and Zliq:

! I could not compile the PDF to copy the needed section

We have also modified Figure 2 to clearly distinguish the fixed-point iteration solver for Eq 11 from the overall ITIC iteration process.

! As stated above, I think we should modify Figure 2

**Comment #16**  
I'm not sure how the authors' comments address the point.  The source of the dashed line is irrelevant.  The error bars on the symbols in figure 8a are too large.

The reviewer’s original comment stated that “fitted lines go right through most of the points”. In our response, we tried to make it clear that the dashed blue lines are not fitted to the open symbols. The reason for large error bars in Figure 8a is that these error bars show the uncertainty of the points during a single run. We replicated these simulations to obtain proper uncertainties.

!Todo: Run replicates or calculate block averages and uncertainties and replot Figure 8a

Try to point out that the reviewer’s original comment stated that “the fitted lines go right through most of the points.” Our response was that these lines are actually not fitted to the data, so they are not evidence for the error bars being too large since the error bars are computed independently.

That being said, the reviewer might have a point that the error bars are too large. For example, shouldn’t the error bars for Tr=1.2 in Figure 8a be of a similar magnitude to those in Figure 9c? Aren’t they computed using similar methods?

If we determine that the Figure 8a error bars are correct, we just need to satisfy the reviewer by stating that we verified that our calculations were correct. And then we should provide some explanation for why they are so large (maybe we only had a few replicates so the 95% confidence interval is quite large).   
  
**Comment #17**  
I don't see how the modifications in section 6 resolves the original issue. The manuscript still indicates that larger systems yield smaller uncertainties ("we need 3200 ethane molecules to achieve low enough uncertainties").

True, I also thought we modified this sentence to make it more clear that this statement only applies to MD rigid?  
! I think I forgot to modify this sentence, but It seems like the reviewer wants us to remove this sentence altogether. How would you modify this sentence to satisfy the reviwer?

We can just focus on the fact that we need 3200 molecules for “reliable” estimates (which is a softer way to imply uncertainties). We really just need to remove the “low enough uncertainties” phrase, but I have tried to reword this sentence:

Figure 9(a) demonstrates that, for the simulation times chosen, 3200 ethane molecules are necessary to obtain reliable estimates of B2 and to match the B2+B3rho + B4rho2 line, which represents the rigorous values of Z-1/rho.

Furthermore, I must express additional confusion about the N=1600 data in Fig 9a, which was previously the least precise (despite being the next-to-largest system size) and now have smaller error bars, but are still much less precise than any other system size.  Why is the N=1600  
data so imprecise?

This is quite bizarre. Any explanation? I tried to give an explanation, but really we just need to say that we verified these error bars.

! I do not have an answer for this. I can repeat these simulations using GROMACS at least for rigid-bond MD to see if the same thing happens.

We acknowledge that the error bars for N=1600 are abnormally large. However, after going back through the data we confirm that these error bars were computed properly. This could possibly be attributed to poor output from one of the four replicates.   
  
**Comment #18**  
It is good that the authors ran longer simulations and determined that issues in Fig 9b are not due to equilibration, but, sadly enough, the manuscript still blames equilibration:  
  
"due to the small number of intermolecular collisions at low density relative to the large number of intramolecular collisions, inhibiting the equilibration of the various components of momentum."  
  
Did the longer simulations give any indications that equilibration was an issue or not?  If not, then the manuscript cannot continue to say that it was.

Did we not mean “equilibration”, but rather “equipartition” or maybe “proper sampling?” The reviewer really doesn’t want us to use the term equilibration, since this suggests that our simulations were simply not long enough or not equilibrated. But I think what we are saying is that the simulation is actually equilibrated but the production output is still not reliable.   
!I think proper sampling is what we should use instead of equilibration.

OK, let’s make that change then.

I am even more confused as to why the compressibility factor (based on the total virial) reported in Fig 15 of the Supplementary Material goes to 0 (and not 1) and why the bonded contributions go to -1.  Is this Z-1 and not Z?

Unfortunately, an older version of Figure 15 caption was mistakenly included. We apologize for the confusion. The total Z approaches 1 at zero density, due to the kinetic energy contribution to compressibility factor. Kinetic energy contribution for this system (not shown in the figure) roughly equals 2 at all densities. Figure 15 in Supplementary Materials is now updated with the caption including a sentence that explains the kinetic energy contribution.

I did not see any modification to Figure 15. Shouldn’t the y-axis be the virial (\Omega) then?

**Comment #20**  
If the error bars can't be added to figure 10, then some description of how big they would still be helpful.  Are they smaller than the symbol size (it looks like they might be in many cases)?  Where they disagree with GEMC/GCMC, is it due to uncertainty or systematic  
deviation?

Could we include the larger error bars? Would most be smaller than the symbol size?

I think we should make the y-range for Figure 10b from -3 to 3 (the y-region of 3 to 6 is not very useful since only one data point is found there).

As a side note, why don’t we ever compare enthalpy of vaporization? We could make Figure 10 a 2x2 plot with the fourth panel for DeltaHv. I am fine not including it in Figure 11 (since these are in the supporting information), but I think people might want to see the comparison with the literature DeltaHv values.

! I think the error bars are actually going to be pretty large, that’s why I hesitate to add them as they crowd the plot significantly.

! Todo: Add DeltaH and change y-axis of Figure 10b

If the conclusions are referring to using REFPROP as input, then it should say so.  "In the absence of simulation uncertainty" is an inadequate indication of this.

The following paragraph in the Conclusions section was modified to clarify that REFPROP data was used as input

