

## Relative resolution: A hybrid formalism for fluid mixtures

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We show here that molecular resolution is inherently hybrid in terms of relative separation. While nearest neighbors are characterized by a fine-grained (geometrically detailed) model, other neighbors are characterized by a coarse-grained (isotropically simplified) model. We notably present an analytical expression for relating the two models via energy conservation. This hybrid framework is correspondingly capable of retrieving the structural and thermal behavior of various multi-component and multi-phase fluids across state space. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4929834>]

### INTRODUCTION

Ever since the days of van der Waals, expressing molecular interactions in terms of short-range and long-range contributions has proven insightful. In such a spirit, it has been recognized that the key signatures of uniform (nonpolar) liquids are mostly unaltered while performing “force truncation” (i.e., meticulously evaluating interactions if molecules are close to each other but effectively neglecting interactions if molecules are far from each other).<sup>1,2</sup> This is because structural correlations are dominated by the fluctuating energetics of nearest neighbors, and thermal properties are corrected by the mean field of other neighbors. Importantly, while the prominent Weeks-Chandler-Anderson (WCA) study has suggested to truncate the force between its repulsive and attractive portions,<sup>3,4</sup> the recent Ingebrigtsen-Schroder-Dyre (ISD) study has argued to truncate it between its primary and secondary coordination shells.<sup>5,6</sup> Nevertheless, for multi-component or multi-phase systems, long-range interactions markedly influence global segregation, as short-range interactions merely affect local packing, and thus, “force truncation” cannot generally describe such nonuniform scenarios. An elegant extension, which constructs a one-body field in a self-consistent way, has been developed; however, this framework mostly deals with idealized nonuniformities (e.g., a planar interface and an isotropic perturbation).<sup>7</sup>

In fact, nonuniform liquids have received much attention by an apparently unrelated community which connects fine-grained (FG) and coarse-grained (CG) models in a variety of ways. Bearing resemblance with various explicit-implicit strategies for describing a medium,<sup>8</sup> Adaptive Resolution contains both FG and CG models in a single system, and it switches between them in terms of absolute position (e.g., a molecule is represented by a FG potential if close to the origin and by a CG potential if far from the origin).<sup>9–12</sup> While such hybrid approaches appear to be computationally useful in examining mixtures, the greatest challenge in these approaches is the

relationship between the FG and CG models. While there are numerous protocols for yielding a CG model given a FG model,<sup>13,14</sup> there is a general consensus between these numerical parametrizations: no model optimally transfers in state space while concurrently representing the structural and thermal behavior of a certain system.<sup>15,16</sup>

In our current work, we present Relative Resolution (Rel-Res): molecules interact with each other via a FG modeling *resolution* at small *relative* separation and via a CG modeling *resolution* at large *relative* separation. While reminiscent ideas have been recently motivated by Adaptive Resolution as well,<sup>17,18</sup> we particularly cast RelRes as an extension of “force truncation.” Besides, the main distinction of our approach is in the means by which we relate the FG and CG potentials. While Ref. 17 numerically parametrizes between the two models (i.e., the squared differences between the respective forces are strictly minimized via molecular simulations), Ref. 18 does not make a clear connection between the two models. We here instead formulate via energy conservation an analytical approximation between the FG and CG potentials. This arithmetic parametrization appears especially pertinent for describing across state space the structural and thermal behavior of nonuniform mixtures. In turn, we present a hybrid strategy that is computationally promising for efficiently evaluating multi-component and multi-phase fluids via molecular simulations.

### THEORETICAL FOUNDATION

Before describing RelRes, we summarize the basics of nonhybrid systems. A CG mixture is frequently composed of single-site molecules, governed by the following energy function:

$$U^{CG} = \frac{1}{2} \sum_{i \neq j} u_{ij}^{CG}(r_{ij}). \quad (1)$$

Corresponding usually with gravitational centers, a particular pair  $i$  and  $j$  interacts via its relative separation  $r_{ij}$  by a CG potential  $u^{CG}$ . A FG mixture is normally composed of

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multi-site molecules, governed by the following energy function:

$$U^{FG} = \frac{1}{2} \sum_{i \neq j} \sum_{\mu_i \nu_j} u_{\mu_i \nu_j}^{FG}(r_{ij} + \Delta r_{\mu_i \nu_j}). \quad (2)$$

Corresponding typically with atomistic coordinates, a particular pair  $\mu_i$  and  $\nu_j$  interacts via its relative separation  $r_{ij} + \Delta r_{\mu_i \nu_j}$  by a FG potential  $u^{FG}$ . In our entire formalism, we ignore intramolecular energetics; our hybrid approach maintains all degrees of freedom, and therefore, intramolecular forces remain unaltered in principle. Also notice that we are allowing for absolute nonuniformity in our mixtures considering the indices on the potentials.

RelRes combines both of the above in the following way:

$$\tilde{U} = \frac{1}{2} \sum_{i \neq j} \left[ \sum_{\mu_i \nu_j} \tilde{u}_{\mu_i \nu_j}^{FG}(r_{ij} + \Delta r_{\mu_i \nu_j}) + \tilde{u}_{ij}^{CG}(r_{ij}) \right]. \quad (3)$$

The focal idea here is that while  $\tilde{u}^{FG}$  is the short-range portion of the FG potential,  $\tilde{u}^{CG}$  is the long-range portion of the CG potential, and we particularly switch between these in the following way, respectively:

$$\tilde{u}_{\mu_i \nu_j}^{FG}(r) = \begin{cases} u_{\mu_i \nu_j}^{FG}(r) - u_{\mu_i \nu_j}^{FG}(r_s) & \text{if } r \leq r_s, \\ 0 & \text{if } r \geq r_s, \end{cases} \quad (4)$$

$$\tilde{u}_{ij}^{CG}(r) = \begin{cases} u_{ij}^{CG}(r_s) & \text{if } r \leq r_s, \\ u_{ij}^{CG}(r) & \text{if } r \geq r_s, \end{cases} \quad (5)$$

where  $r_s$  is the distance at which the short-range and long-range information is switched on or off. Note that  $U^{FG} = \tilde{U}(r_s \rightarrow \infty)$  and  $U^{CG} = \tilde{U}(r_s \rightarrow 0)$ .

We now seek a relationship between the FG and CG potentials. RelRes naturally accounts for the FG interactions at small separations, and thus, we solely require a parametrization for the CG interactions at large separations. For this purpose, we consider the two nonhybrid systems as defined by Eqs. (1) and (2): if each has merely two molecules at essentially infinite separation,  $U^{CG} = u_{ij}^{CG}(r_{ij})$  and  $U^{FG} = \sum_{\mu_i \nu_j} u_{\mu_i \nu_j}^{FG}(r_{ij} + \Delta r_{\mu_i \nu_j})$ , respectively; in turn, these energy functions can be approximately equated with each other while taking the appropriate limit of the latter,  $r_{ij} \gg \Delta r_{\mu_i \nu_j}$ ,

$$u_{ij}^{CG}(r) \approx \sum_{\mu_i \nu_j} u_{\mu_i \nu_j}^{FG}(r). \quad (6)$$

Based on energy conservation, this equation can analytically parametrize from a FG model to a CG model, and for the remainder of our work, we term it as *the Molecular Pair in the Infinite Limit* (MPIL). Notice that  $r_{ij} \gg \Delta r_{\mu_i \nu_j}$  is alternatively satisfied by vanishing molecular dimensions (e.g., setting all bonds at a distance of zero); with the FG atomistic coordinates collapsing onto the CG gravitational centers, MPIL geometrically translates as the summation of all potentials as if they isotropically connect only two points. MPIL can be also realized as the monopole term of a multipole expansion; obviously for (neutral) polar molecules, this is strictly zero, suggesting in turn that dipolar orientation may be crucial for charged systems even at infinite separation. We restrict the remainder of our work to nonpolar molecules.

Suppose that the FG and CG potentials can be each cast as a linear combination of basis functions,  $u_{\mu_i \nu_j}^{FG}(r) = \sum_m c_{m, \mu_i \nu_j}^{FG} f_m^{FG}(r)$  and  $u_{ij}^{CG}(r) = \sum_m c_{m, ij}^{CG} f_m^{CG}(r)$ , respectively. Here,  $m$  is the index of the basis function  $f_m$ , and  $c_m$  is its respective coefficient. Substituting these expressions in Eq. (6), we make the following observations:

$$f_m^{CG}(r) \approx f_m^{FG}(r), \quad (7)$$

$$c_{m, ij}^{CG} \approx \sum_{\mu_i \nu_j} c_{m, \mu_i \nu_j}^{FG}. \quad (8)$$

These approximations, respectively, mean that the basis functions of the CG model shall be the same as those of the FG model, and that the CG coefficients can be sequentially estimated by elementary arithmetics of the FG coefficients. While these expressions are completely general, we now specialize to the Lennard-Jones (LJ) potential in all that follows. As a rudimentary example, consider a system of identical molecules, each having  $n$  identical sites. Not only does MPIL impose LJ functionality for all interactions, but it also relates between the length and energy parameters,  $\sigma^{CG} \approx \sigma^{FG}$  and  $\epsilon^{CG} \approx n^2 \epsilon^{FG}$ , respectively. In Fig. 1, we exemplify RelRes with MPIL for this scenario, particularly having two variations for  $r_s$ : one is motivated by Ref. 3 (i.e.,  $r_{WCA} \equiv 2^{1/6} \sigma$ , dotted curves), while another is inspired by Ref. 5 (i.e.,  $r_{ISD} \equiv 2^{2/3} \sigma$ , dashed curves); we continue examining these alternatives for  $r_s$  throughout our investigation.

## COMPUTATIONAL VALIDATION

In the remainder of our work, we notably focus on the ability of our hybrid approach in describing *reference mixtures* (i.e., systems with just FG and no CG interactions). For this task, we invoke molecular simulations:<sup>19</sup> in all cases, we proceed in time via the leap-frog algorithm, while maintaining a density  $\rho$  and a temperature  $T$  via canonical sampling.<sup>20</sup> By introducing in RelRes a four-term polynomial between  $r_s - \delta r_s$  and  $r_s + \delta r_s$ , we guarantee continuity not only in the potential but also in the force: we specifically use  $\delta r_s = 0.0000\sigma$  for  $r_s = r_{WCA}$  and  $\delta r_s = 0.0625\sigma$  for  $r_s = r_{ISD}$ . Analogously, we switch all potentials off between  $2.25\sigma$  and  $2.75\sigma$ , employing tabulated functions throughout for purposes of implementation. Importantly, we assume that all parameters

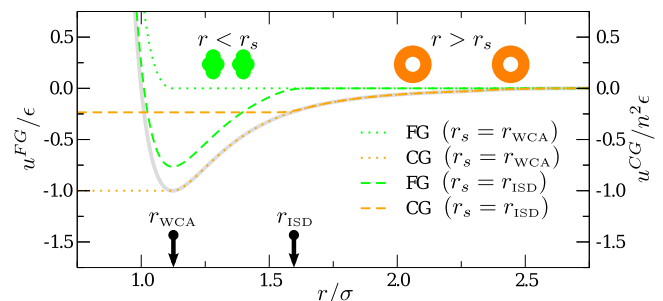


FIG. 1. Variations of FG (green curves, left ordinate) or CG (orange curves, right ordinate) potentials in terms of the relevant distance. We nondimensionalize by the parameters of the former model throughout; specifically here,  $n$  corresponds with an arbitrary integer. The molecular schematics essentially portray the appropriate regions of nonzero force. The solid (gray) curve is for the full LJ potential.

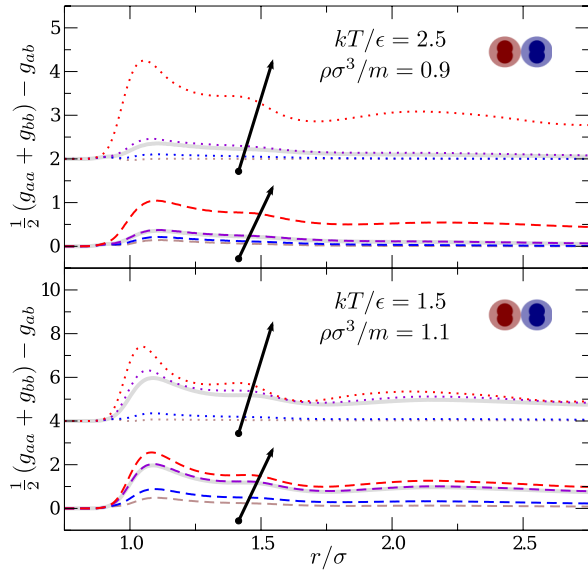


FIG. 2. Radial distributions for the dumbbell scenario in terms of the relevant distance. In each panel, the top (dotted) set is for  $r_s = r_{\text{WCA}}$ , and the bottom (dashed) set is for  $r_s = r_{\text{ISD}}$ ; the former is shifted upwards by an arbitrary integer. The gray (solid) curve is for the reference mixture, and it is duplicated between the sets; this coding is maintained throughout our work. Arrows point in the direction of increasing  $\lambda$ .

of the reference fluids are constant in state space, which readily means by MPIL that all parameters in RelRes are analogously constant.

For a preliminary examination, we construct a binary dumbbell mixture with  $n = 2$  for each type. Depicted in Fig. 2, each molecule is chemically homogenous: two FG  $a$  sites map on one CG  $\mathcal{A}$  site, and two FG  $b$  sites map on one CG  $\mathcal{B}$  site. Each actual FG site has mass  $m$ , and each virtual CG site has mass zero. We purposefully set the conditions of the reference mixture so as to yield a segregation between two liquids in ample time. We rigidify each bond at a distance of  $0.5\sigma$ , and the LJ potential with geometric mixing is the basis for all interactions. We set the length parameters with  $\sigma_{aa}^{\text{FG}} = \sigma$  and  $\sigma_{bb}^{\text{FG}} = \sigma$ , and we set the energy parameters with  $\epsilon_{aa}^{\text{FG}} = (1 + \sqrt{5})\epsilon/2$  and  $\epsilon_{bb}^{\text{FG}} = 2\epsilon/(1 + \sqrt{5})$ . Importantly,  $\sigma_{ij}^{\text{CG}} = \sigma_{\mu_i\nu_j}^{\text{FG}}$ , as well as  $\epsilon_{ij}^{\text{CG}} = \lambda\epsilon_{\mu_i\nu_j}^{\text{FG}}$ , with  $\lambda$  being a tuning parameter which allows us to systematically examine the hybrid approach (i.e.,  $\lambda = 0$  expresses “force truncation,” and  $\lambda = 4$  retrieves MPIL parametrization).  $k$  throughout is Boltzmann’s constant, and further information is given in the caption of Fig. S1.<sup>21</sup>

We focus foremost on the ability of the hybrid systems in describing structural correlations as manifested by radial distributions,  $g$ . We present various combinations of these functions in Fig. 2 here, as well as in Fig. S1.<sup>21</sup> Unsurprisingly in either panels, the traditional variation of “force truncation,” as manifested by  $\lambda = 0$  with  $r_s = r_{\text{WCA}}$  (i.e., dotted brown curve), is completely inadequate in describing the various  $g$ , particularly lacking any evidence of a phase segregation. Having only short-range repulsions, the various sites appear almost identical between each other at separations closer than  $r_{\text{WCA}}$ , and as such, they have a similar preference for each other in terms of structure. Keeping  $\lambda$  constant while lengthening  $r_s = r_{\text{ISD}}$  (i.e., dashed brown curve), we still cannot attain a

sufficient representation of the phase segregation, suggesting in turn that energetics beyond  $r_s$  may be necessary. Eminently in either panels, the parametrization of MPIL, as exemplified by  $\lambda = 4$  with  $r_s = r_{\text{ISD}}$  (i.e., dashed violet curve), is excellently capable of retrieving the various  $g$ , especially capturing all signatures of the phase segregation. It appears that the CG sites effectively correct for the FG sites in their long-range attractions, advocating that at separations beyond  $r_{\text{ISD}}$ , an isotropic assumption for molecules sufficiently describes the relevant forces. Keeping  $\lambda$  constant while shortening  $r_s = r_{\text{WCA}}$  (i.e., dotted violet curve), we cannot anymore attain a flawless representation of radial distributions, suggesting in turn that geometrical intricacies of all nearest neighbors may be vital for structure. Furthermore, MPIL parametrization is validated as we perturb it off its ideal value: For either value of  $r_s$ , the hybrid system of RelRes is under-segregated for  $\lambda = 2$  (i.e., blue curves) and over-segregated for  $\lambda = 6$  (i.e., red curves), as compared with the reference mixture. Although CG models cannot, in general, replicate the structure of FG models, RelRes does not encounter this issue as it makes a valid approximation beyond  $r_s$  via MPIL.

We now correspondingly examine thermal properties in Fig. 3: by the virial approach, we compute the pressure,  $P$ , and by inspecting adjacent densities, we also evaluate the modulus,  $K$  (i.e., the inverse of the compressibility). Importantly, these two cannot be concurrently retrieved for a FG system by a CG system, but this is not the case for RelRes. For either  $r_s$ , both decrease almost linearly with increasing  $\lambda$ , and each set crosses its reference value at a single location (i.e.,  $\lambda$  of MPIL). RelRes naturally maintains the energetics between near neighbors, and it also appears that via MPIL, it correctly describes the energetics between far neighbors; consequently, our hybrid approach can retrieve these thermal properties for the reference mixture. We also note here that the sets of  $r_s = r_{\text{ISD}}$  (i.e., circles) consistently yield better replication than the sets of  $r_s = r_{\text{WCA}}$  (i.e., diamonds).

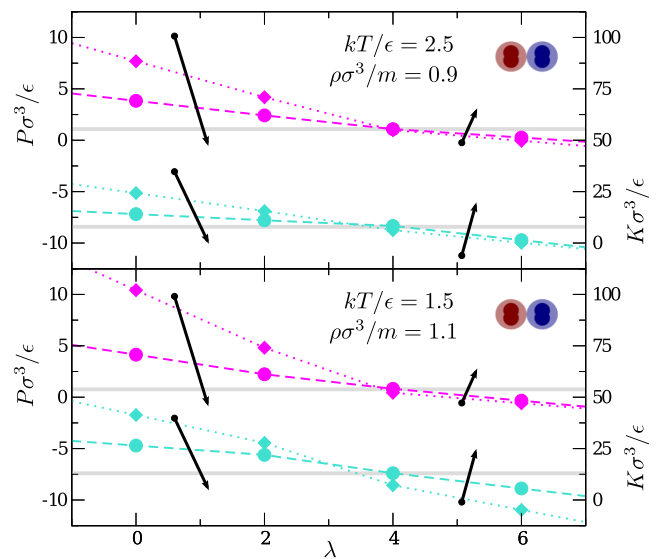


FIG. 3. Sets of pressure (magenta symbols, left ordinate) and modulus (turquoise symbols, right ordinate) for the dumbbell scenario in terms of the tuning parameter. Arrows point in the direction of increasing  $r_s$ , and otherwise, these curves are in the spirit of Fig. 2.

Importantly, this entire analysis involves two different sets of temperature and density, as manifested by the panels of both Figs. 2 and 3. As such, it appears that RelRes with MPIL is transferable across  $kT/\epsilon$  and  $\rho\sigma^3/m$  of order unity, sufficiently representing the structural and thermal behavior of the reference mixture in this region. While CG models cannot be optimally transferable for FG models throughout state space, RelRes avoids such issues via MPIL. Transferability may stem in the fact that Eq. (6) contains no state parameters. Perhaps, state functionality is involved in  $r_s$ , but we do not observe such subtleties here. Regardless, we must emphasize that RelRes with MPIL is only necessary for mixtures; for uniform liquids, “force truncation” together with a mean field is usually sufficient, and we exemplify this via another dumbbell scenario which is described in Fig. S2.<sup>21</sup>

Nevertheless, can RelRes with MPIL successfully describe realistic mixtures as well? Demonstrating that this is in fact the case, we devise a binary star-ring system with  $n = 5$  for each type. Depicted in Fig. 4, each molecule is chemically heterogeneous: shaped like a regular tetrahedron and representative of tetrachloromethane, CG  $\mathcal{A}$  has at its center one FG  $b$ , and it is bonded with four FG  $a$ , which are not bonded between each other. Shaped like a regular pentagon and representative of thiophene, CG  $\mathcal{B}$  has in total one FG  $a$  and four FG  $b$ , and each of these is bonded with another two of these. We purposefully set the conditions of the reference mixture so as to yield an instability with a cavity. We again rigidify each bond at a distance of  $0.5\sigma$ , setting all other intramolecular potentials identical with their intermolecular counterparts. We specifically focus here on MPIL parametrization (i.e.,  $\sigma_{\mathcal{A}\mathcal{A}}^{CG} = \sigma_{aa}^{FG}$  and  $\sigma_{\mathcal{B}\mathcal{B}}^{CG} = \sigma_{bb}^{FG}$ , as well as  $\epsilon_{\mathcal{A}\mathcal{A}}^{CG} = 16\epsilon_{aa}^{FG} + 8\epsilon_{ab}^{FG} + \epsilon_{bb}^{FG}$  and  $\epsilon_{\mathcal{B}\mathcal{B}}^{CG} = \epsilon_{aa}^{FG} + 8\epsilon_{ab}^{FG} + 16\epsilon_{bb}^{FG}$ ), comparing it in turn with “force truncation;” notice that because of molecular complexity, we do not have here scaling relations for all parameters. Otherwise, we proceed in a reminiscent manner as in the dumbbell protocol, and further information is given in the caption of Fig. S3.<sup>21</sup>

We present various combinations of radial distributions in Fig. 4 here, as well as in Fig. S3;<sup>21</sup> the caption of the latter also correspondingly lists values for pressure and modulus. Overall, RelRes with MPIL at  $r_s = r_{\text{ISD}}$  successfully describes the structural and thermal behavior of the reference fluid, and this

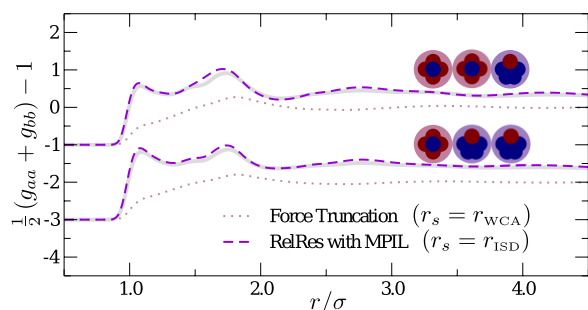


FIG. 4. Radial distributions for the star-ring scenario in terms of the relevant distance. While these curves are in the spirit of Fig. 2, they are, indeed, for  $kT/\epsilon = 2.0$  and  $\rho\sigma^3/m = 1.0$ . Corresponding with the ratio depicted above each set, the top set has a composition dominated by stars, and the bottom set has a composition dominated by rings; the latter is shifted downwards by an arbitrary integer.

is especially notable as compared with “force truncation” at  $r_s = r_{\text{WCA}}$ , which mistakenly predicts a stable mixture with no cavity. With this hybrid approach, molecules can readily distinguish between a liquid droplet and a gas bubble at a certain distance, since they naturally capture the energetics of their near and far neighbors. While this argues for the transferability across both gaseous and liquid phases, RelRes with MPIL is also transferable across different compositions, since we vary the concentration in this tetrachloromethane-thiophene scenario. Besides, the instability here suggests that this hybrid framework can be applied beyond equilibrium. Finally, we construct another star-ring scenario which is described in Fig. S4;<sup>21</sup> we consequently show that even with further complications between the parameters, the hybrid approach can still be robustly employed.

## CONCLUSION

Our current work presents a hybrid picture for fluid mixtures, in which the resolution of a certain molecule is relatively defined in terms of its observer: while the geometrical intricacies of nearest neighbors are crucial for consideration, other neighbors may be characterized as isotropic points. We have demonstrated this idea by introducing here two distinct concepts, the framework of RelRes and the parametrization of MPIL, which are ideal if employed together. RelRes sets the general Hamiltonian for switching between the FG and CG resolutions in terms of relative separation between molecules, and MPIL provides the relationship between these two (i.e., Eq. (6)). As such, RelRes with MPIL is capable of retrieving across state space not only the structural correlations but also the thermal properties (e.g., pressure and compressibility) of the multi-component and multi-phase fluids which we have investigated here (e.g., a generic tetrachloromethane-thiophene mixture). Importantly, it appears that the analytical nature of MPIL is crucial in the transferability of our hybrid approach, especially since Refs. 17 and 18 are unsuccessful in this regard. Finally, it is rather remarkable that at least for the fluids considered here, the infinite limit involved in our formalism is virtually satisfied just beyond nearest neighbors.

On a practical level, our hybrid approach presents a useful tool in exploring the behavior of mixtures. Except that RelRes notably diminishes the number of interactions necessary for computation beyond  $r_s$ , the analytical parametrization of MPIL allows for trivial transferability across state space. As a next step, it may be of value to incorporate some of these ideas in Adaptive Resolution.

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