Evaluation of criticality from molecular models using the virial equation of state

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Recent developments permit the calculation of virial coefficients up to about B6 for complex multiatomic molecular models. This development provides a potential route to the estimate of the critical point for a molecular model. The ability to do this depends on how well the virial equation of state (VEOS) remains valid as the critical density is approached. Although the critical point is singular in nature, and the behavior near it cannot in principle be described with an analytic equation such as the VEOS, we find that in applying this approach a useful estimate of its location can be found for some systems. We demonstrate this with several examples, including the Lennard-Jones model, binary Lennard-Jones mixtures, TraPPE alkanes, and a polarizable model of water. The approach is effective for non-polar molecules, but further developments are needed to enable it to be applied to polar molecules such as water.