How to make an equation of state

Simulations have become an increasingly important tool in research and development. In the world of computational fluid dynamics, the equation of state fulfills the central role of determining the properties of the gas or liquid, for example its pressure or energy at some temperature and density. The ideal gas law is the simplest equation of state for gases. It states that the pressure times volume is constant for some amount of gas at a constant temperature. This is only an approximation, ignoring the size of the molecules and all forces between them. Obviously, the approximation doesn't work when the particles are tightly packed, so in order to get a good afternoon weather forecast on Jupiter, a more complicated model is needed. A better gas law can also be used to develop a new rocket engine design, or determine the properties of a new rocket fuel or explosive without any chemist needing to synthesise it.

It is not necessarily very difficult to create a new equation of state. Robert Boyle was able to determine that the pressure of air is inversely proportional to its volume through simple experiments as early as 1662. Measuring how the gas behaves at such extreme conditions as in a detonation turns out to be quite tricky though. Not to mention that measurement equipment is not usually explosion proof. Therefore I chose a more theoretical and microscopic approach to an equation of state, based on the molecular interactions the ideal gas law so delightfully ignores. There are many more or less realistic models for gas molecules, and the one I used is the so-called exponential-6 potential. The name comes from the exponentially increasing repulsion between two molecules that are forced together, and the short range attraction which falls off with the distance between the molecules to the power of six.

The best way to go from a model of a pair of molecules to a well-determined gas behaviour is ironically a computer method based on randomness: Monte Carlo. The idea is to put a few hundred molecules in a small box, and then generate particle configurations that look like snapshots of a real gas in motion. Then, the average properties can be calculated from thousands or millions of different configurations. So how are realistic configurations generated? Simply placing the particles randomly in the box and then determining how likely they are to occur would work in theory, but not in practice. The problem is that most configurations in a dense gas are extremely unlikely to occur. In fact, the probability to randomly pick a valid configuration for 100 hard-sphere particles at their freezing point is one in 10^{260}, so spectacularly unlikely that all computers on earth would fail even if they had a billion years. A less extreme analogy could be to try to determine the average depth of Öresund by measuring at random locations around the world. Obviously, most measurements would contribute nothing and be a huge waste of time. A more sensible approach is to start in Öresund itself. Since we don't know exactly where the water ends in advance (we don't have a map), we then take random steps and add each new measurement to the average. If a move lands on land, it is simply rejected and the next step proceeds from the previous position. This is the idea behind the Metropolis Monte Carlo algorithm — particles in the box are initially arranged in a valid configuration and then subjected to trial moves one by one, which are accepted or rejected based on how much energy they cost. After each move, the properties of the current configuration such as pressure and energy are added to the average. A few million steps are enough to get very accurate averages, as good as experimental data.

While Monte Carlo calculations are accurate, it is far from a fast method. Therefore, the new equation of state is simply a long polynomial fitted to the results of 16000 Monte Carlo calculations that were run on a supercomputer. It is the best of two worlds - a numerically efficient equation that can be calculated at lightning speed by a computer, combined with the near perfect accuracy of Monte Carlo. The idea of fitting a polynomial to a complex model is nothing new, but this gas law achieves considerably better results using only a tenth of the polynomial coefficients that previous equations use.

The new gas law works on room temperature air of course, but it truly shines when it comes to gases at extremely high pressures. It was for example able to determine the properties of water vapour compressed to over a million times atmospheric pressure, a third of the pressure in the earth's core. With a density higher than concrete, the water was only kept gaseous due to its high temperature, twice as high as the surface of the sun. This ability to quickly and accurately predict gas behaviour under extreme conditions will in the future save researchers and engineers both time and computational resources, whether it be rocket propulsion research or energetic material design.