

8.6: The Hard Sphere Fluid

Consider a fluid in which each atom is modeled by a “hard sphere” of volume v_0 . In this system the potential energy vanishes unless two spheres overlap, while if they do overlap it is infinite. The criterion for overlap is that the centers of the two spheres are separated by a distance of $2r_0$ or less, where $v_0 = \frac{4}{3}\pi r_0^3$. This model is certainly oversimplified in that it ignores the attractive part of the interatomic force, but it is an excellent starting point for perturbation theory, and it also has certain features of interest in its own right, as the problems below demonstrate. (The first problem below is required background for all of the others.)

8.12 Scaling in the hard sphere fluid

The canonical partition function for a fluid is

$$Z(T, V, N) = \frac{1}{\lambda^{3N}(T)N!} \int d^3r_1 \cdots \int d^3r_N e^{-\beta U_N(\mathbf{r}_1, \dots, \mathbf{r}_N)}. \quad (8.6.1)$$

For an ideal gas, the integral over configuration space gives just V^N , so it makes sense to write

$$\begin{aligned} Z(T, V, N) &= \left(\frac{V^N/N!}{\lambda^{3N}(T)} \right) \left(\frac{1}{V^N} \int d^3r_1 \cdots \int d^3r_N e^{-\beta U_N(\mathbf{r}_1, \dots, \mathbf{r}_N)} \right) \\ &\equiv Z_{\text{ideal}}(T, V, N) W(T, V, N), \end{aligned} \quad (8.6.2)$$

where the last line has defined W , the ratio of interacting to non-interacting (“ideal”) configurational partition functions.

- Argue that in the case of hard spheres W is independent of temperature. It does, however, depend on the mechanical parameter v_0 , so we will write the ratio as $W(V, N, v_0)$.
- Argue that $W(V, N, v_0) \leq 1$, where the equality holds only when $v_0 = 0$.
- Show that the Helmholtz free energy for any fluid satisfies

$$\begin{aligned} F_{\text{HS}}(T, V, N, v_0) &= F_{\text{ideal}}(T, V, N) - k_B T \ln W(V, N, v_0) \\ &\equiv F_{\text{ideal}} + N f_{\text{ex}}, \end{aligned} \quad (8.6.3)$$

where we have defined f_{ex} , the excess free energy per atom. Is the free energy of a hard sphere fluid greater than or less than the free energy of an ideal gas at the same T , V , and N ?

- Because f_{ex} is intensive, it cannot depend upon V and N separately, but only through their intensive quotient, the number density $\rho = N/V$. Use a similar argument to show that

$$W(V, N, v_0) = w(\rho, v_0)^N, \quad (8.6.4)$$

where w is a dimensionless, intensive quantity.

- Use dimensional analysis to show that the hard sphere w (and hence f_{ex}) cannot depend upon ρ and v_0 separately, but only through their product: $w(\rho v_0)$.

This last result is of enormous importance. It implies that there is no need to perform elaborate computer simulations for a variety of densities and a variety of radii. It suffices to either simulate for a variety of densities at one fixed radius or vice versa. It also demonstrates that the quantity of importance in the statistical mechanics of hard spheres is the “scaled density” $\eta \equiv \rho v_0$.

- Use thermodynamics to show that

$$p_{\text{HS}}(T, \rho, v_0) = p_{\text{ideal}}(T, \rho) + \rho \left[\eta \frac{\partial f_{\text{ex}}(\eta)}{\partial \eta} \right]_{\eta=\rho v_0}. \quad (8.6.5)$$

8.13 The hard sphere phase transition

- Interpret the scaled density $\eta \equiv \rho v_0$ geometrically. Why is it sometimes called the “packing fraction”?
- Is it possible to have a fluid with $\eta \geq 1$?
- Show that if hard spheres are packed into a face-centered cubic lattice (which is probably the densest possible packing spheres, although no one has been able to prove it), $\eta = \pi\sqrt{2}/6 = 0.7405$.

In fact, at scaled densities η well below the limits mentioned above, the system undergoes a phase transition from a fluid to a solid. Computer simulations show that the transition occurs when the scaled density is $\eta_t \approx 0.496$. The conjecture $\eta_t = \frac{1}{2}$ is tempting, but apparently not correct. (On the other hand it is hard to do computer simulations near phase transitions, so the question is not completely closed!)

8.14 The hard sphere fluid equation of state

Many long and difficult hours of analytic calculation and computer simulation have gone into studying the hard sphere fluid. In 1964 Ree and Hoover¹ codified much of this work into the following empirical formula which is a good approximation for the hard sphere fluid equation of state:

$$p_{\text{HS}}(T, \rho, v_0) = k_B T \rho \left[1 + 4\eta \frac{1 + 0.25403\eta + 0.27726\eta^2}{1 - 2.2460\eta + 1.3010\eta^2} \right] \quad \text{where} \quad \eta = \rho v_0. \quad (8.6.6)$$

Only five years later, Carnahan and Starling² hit upon a much simpler yet still remarkably accurate equation of state, namely

$$p_{\text{HS}}(T, \rho, v_0) = k_B T \rho \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad \text{where} \quad \eta = \rho v_0. \quad (8.6.7)$$

Both of these formulas apply only to the fluid phase (see the previous problem) and neither one is exact. Answer the following questions for the Carnahan-Starling formula.

- As the density increases from zero, at what point does the formula become nonsense?
- On which regions of the (T, ρ) plane does the hard sphere fluid exert a greater pressure than the ideal gas? Can you explain your answer through a simple physical argument?
- Integrate equation (8.56) to show that for the hard sphere fluid,

$$f_{\text{ex}}(T, \eta) = k_B T \eta \frac{4 - 3\eta}{(1 - \eta)^2}. \quad (8.6.8)$$

Does this formula satisfy the inequality established in part (c.) of problem 8.12?

- Find the difference between the entropy of the hard sphere fluid and that of an ideal gas. At a given T , V , and N , which entropy is larger? Can you justify this result with a qualitative argument?

8.15 The hard sphere free energy

Use the Gibbs-Bogoliubov inequality to show that

$$F_{\text{HS}}(T, V, N) \geq F_{\text{ideal}}(T, V, N). \quad (8.6.9)$$

Reason that $E_{\text{HS}}(T, V, N) = E_{\text{ideal}}(T, V, N)$, and conclude with a relation between entropies.

8.16 Virial expansion for hard spheres

Using the notation of problem 8.12, show that for a hard sphere fluid:

- $Q_2 = \frac{1}{2} V(V - 8v_0)$.
- $b_2 = -4v_0$.
- $B_2(T) = 4v_0$.
- Show that both the Ree-Hover and the Carnahan-Starling equations of state, introduced in problem 8.14, expand to give the correct first virial coefficient $B_2(T)$.

¹F.H. Ree and W.G. Hoover, *J. Chem. Phys.*, **40** (1964) 939–950.

²N.F. Carnahan and K.E. Starling, *J. Chem. Phys.*, **51** (1969) 635–636.