

## 8.1: Introduction

The subject of this chapter is also called “real gases”, or “dense gases”, or “non-ideal gases”, or “imperfect gases”, or “liquids and dense gases”. The many names are a clue that the same problem has been approached by many different scientists from many different points of view, which in turn is a hint that the problem is one of enormous importance. And in this case the hints are correct. We have treated non-interacting classical atoms for long enough in this book. We know that this treatment leads to results in which all substances have the same equation of state (although they can sometimes be distinguished through their heat capacities) and in which there are no phase transitions, no crystals, no life, and very little of interest. It galls me that anyone ever called such a situation “ideal”. The problem of interacting atoms is important for industrial and military applications, but it is just as important from the point of view of pure science. We are now going to see what happens when we allow the atoms to interact. Some call the methods and results “messy”. I call them fascinating. I would not want to live in the “ideal” world.

To be specific, we will consider the model problem of:

- *Monatomic* atoms with no internal structure, interacting through spherically symmetric pair potentials.
- *Classical mechanics*.

Many undergraduate books state that this is an “important outstanding problem”. That is no longer correct. In fact, the problem was solved (except near phase transitions) in the years 1980–85 by Lado, Ashcroft, Foiles, and Rosenfeld (see Talbot, Lebowitz, *et al.* “A comparison of MHNC and MC at high pressures”, *J. Chem. Phys.* **85** (1986) 2187–2192, Y. Rosenfeld, “Variational MHNC”, *J. Stat. Phys.* **42** (1986) 437–457). The solution is a technique called “modified hyper-netted chain”. Unfortunately, I will not have time to tell you what the solution is or even what the words in the name mean. But I can tell you that it is an ingenious combination of perturbation and variational methods, and I will be telling you about these two techniques in this chapter. (The best references for this chapter are the books by Donald McQuarrie, *Statistical Mechanics*, and by J.P. Hansen and I.R. McDonald, *Theory of Simple Liquids*.)

### Problems

#### 8.1 The Lennard-Jones potential

The general Lennard-Jones potential is

$$u(r) = -\frac{a}{r^6} + \frac{b}{r^n} \quad (8.1.1)$$

- Given  $a$  and  $b$ , find  $\epsilon_m$ , the minimum energy, and  $r_0$ , the distance of separation at that minimum. Write  $u(r)$  in terms of the parameters  $\epsilon_m$  and  $r_0$  rather than the parameters  $a$  and  $b$ .
- If  $\sigma$  is the separation at which  $u(\sigma) = 0$ , find  $\sigma$  in terms of  $r_0$ . Why is  $\epsilon_m$  irrelevant here?
- Note the simplifications in the above results if  $n = 12$ . For this case, write  $u(r)$  using the parameters  $\epsilon_m$  and  $\sigma$ .

#### 8.2 Negative compressibilities

Look at figure 8.6.1 on page 307 of Reif. Notice that for temperatures below the critical temperature ( $T_4$  in the figure), the van der Waals fluid can have negative values of  $\kappa_T$ . Suppose a fluid with negative compressibility existed, and I had a bottle of it on the table in front of me. What would happen if the volume of the bottle decreased slightly. . . say if I rapped my fingers on it? (This impossibility is a warning that the van der Waals equation is simply not applicable at temperatures in the vicinity of the critical temperature or below.)

#### 8.3 Entropy of a real gas

A real gas obeys the equation of state

$$pV = Nk_B T \left[ 1 + B \frac{N}{V} \right], \quad (8.1.2)$$

where  $B$  is a positive constant.

- In one sentence, describe the behavior of this gas in the limit that  $T$  and  $N$  are constant but  $V \rightarrow \infty$ . (Answers containing mathematical symbols are automatically disqualified.)

- b. Using an appropriate Maxwell relation, calculate the difference in entropy between an ideal gas and this real gas when both have the same  $T$ ,  $V$ , and  $N$ .
- c. At a given  $T$ ,  $V$ , and  $N$ , which entropy is larger? Is this consistent with “the entropy inequality”? Can you justify it with a qualitative argument? Is it possible for the constant  $B$  to be negative or zero?

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