Lecture 33 - Non-ideal classical gases

What's Important:

- non-ideal classical gases
- virial coefficient

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Non-ideal classical gases

The previous two lectures on phase transitions have dealt with quantized spins on a lattice. We now move to the continuum problem of phase transitions in a non-ideal gas - that is, a gas of interacting particles.

The total energy for a broad category of interaction models can be expressed as

$$H = K + U = (1/2m)\, \Sigma_i p_i^2 + \Sigma_{j\neq k} u_{jk}(\mathbf{r}_{jk}) \qquad (33.1)$$

where the momentum dependence is contained in the kinetic energy term and the coordinate dependence is in the potential energy term (*of course, there exist situations in which the interactions are momentum-dependent too*).

For example, the "6-12" Lennard-Jones potential is of the form

$$u(r) = u_o \left[\left(\frac{R}{r}\right)^{12} - 2\left(\frac{R}{r}\right)^{6} \right]$$

where u_o and R are parameters. This potential is strongly repulsive at short range, and weakly attractive at long range. Because of the separation of the Hamiltonian into position and momentum components, the partition function factors as well:

$$\begin{aligned} Z &= \frac{1}{N!}\frac{1}{h^{3N}} \int e^{-\beta(K+U)} d^3p_1..d^3p_N d^3r_1..d^3r_N \\ &= \frac{1}{N!}\frac{1}{h^{3N}} \int e^{-\frac{\beta}{2m}(p_1^2+..p_N^2)} d^3p_1...d^3p_N \int e^{-\beta U(r's)} d^3r_1...d^3r_N \end{aligned} \qquad (33.2)$$

where the leading $N!$ arises because the particles are classical, but distinguishable.

We have evaluated the momentum part of the partition function some time ago when we did the ideal gas, where we established that it factored into N identical terms like

$$\int e^{-\frac{\beta}{2m}p^2} d^3p = (2\pi m k_B T)^{3/2} .$$

Thus,

$$Z = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} Z_u \qquad (33.3)$$

where

Z_U ~ [*coordinate space integrals*]

Now, if all the $u(r)$ terms vanish, as they do for non-interacting particles, then $Z_U \rightarrow V^N$, as before, and we recover the ideal gas law. The question is, how do we calculate Z_U when the potential energy $U(r_1...r_N)$ does not cleanly separate out into a sum of terms like

$$U(r_1...r_N) \qquad ?? \text{ -> } ?? \qquad u(r_1) + ... + u(r_N).$$

In this case, we can obtain an approximate expression for Z_U in the low density limit by the following procedure.

We expand $\ln Z_U(ß)$ about $ß$=0 in a Taylor sense by writing

$$\ln Z_U(ß) = \ln Z_U(ß = 0) + \int_0^{ß} \frac{\partial \ln Z_U(ß')}{\partial ß'} dß'$$

The first term on the right hand side is easy to evaluate: at zero temperature, the interaction contributions vanish and we have

$$Z_U(ß=0) = V^N \rightarrow \qquad \ln Z_U(ß=0) = N \ln V.$$

The integrand in the second term is just a generalization of a result obtained before for discrete states, namely

$$\bar{U}(ß') = \frac{\int U e^{-ßU} d^3r_1..d^3r_N}{\int e^{-ßU} d^3r_1..d^3r_N} = -\frac{\partial}{\partial ß} \ln Z_U(ß)\bigg|_{ß'}.$$

With these substitutions, we have

$$\ln Z_U(ß) = N \ln V - \int_0^{ß} \bar{U}(ß') dß'. \qquad (33.4)$$

To use this expression, we have to determine the mean potential energy as a function of temperature. In the low density regime, the average potential energy of the ensemble of N particles is just the pairwise sum of individual potential energies: *i.e.*,

$$U = u_{1,2} + u_{1,3} + ... + u_{N-1,N},$$

so that the integral over the exponential gives

$$\int e^{-ß(u_{1,1} + u_{1,2}...)} (d^3r)^N \rightarrow \sum_{pairs} \int e^{-ßu} d^3r$$

This tells us that

$$\bar{U} = \frac{1}{2} N(N-1)\bar{u} \quad \frac{N^2}{2} \bar{u} \qquad (33.5)$$

where the factor $N(N\text{-}1)/2$ arises from the number of pairs, and $\bar{u}$ is the mean of a single u. To emphasize,

$$\bar{U} \neq N\bar{u}$$

The individual $\bar{u}$ is dominated by two-body interactions in the low-density regime, there being very little likelihood of three-body interactions. Thus

$$\bar{u} = \frac{\int u e^{-\beta u} d^3 r}{\int e^{-\beta u} d^3 r}$$

where

- u is a two-body interaction, so
- r is a two-particle separation vector.

Now, $u(r)$ falls off very rapidly with distance, so $e^{-\beta u}$ is of the order unity over most of its integration range. Hence, we try

$$\int e^{-\beta u} d^3 r = \int [1 + (e^{-\beta u} - 1)] d^3 r$$

$$= \int d^3 r + \int (e^{-\beta u} - 1) d^3 r$$

$$= V + I(\beta)$$

$$= V\left(1 + \frac{I}{V}\right)$$

where

$$\int (e^{-\beta u} - 1) d^3 r = I(\beta).$$

Given its definition, at low temperatures $I(\beta)$ is small compared to unity, a property which we now exploit to obtain an approximate expression for $\bar{u}$. Returning to its definition,

$$\bar{u} = \frac{\int u e^{-\beta u} d^3 r}{\int e^{-\beta u} d^3 r} = -\frac{\partial}{\partial \beta} \ln\left[\int e^{-\beta u} d^3 r\right]$$

$$= -\frac{\partial}{\partial \beta}\left[\ln V + \ln\left(1 + \frac{I}{V}\right)\right]$$

$$= 0 - \frac{\partial}{\partial \beta} \ln\left(1 + \frac{I}{V}\right)$$

$$= -\frac{1}{\left(1 + \frac{I}{V}\right)} \frac{\partial}{\partial \beta}\left(1 + \frac{I}{V}\right)$$

$$-\frac{1}{(\sim 1)} \frac{\partial}{\partial \beta}\left(\frac{I}{V}\right)$$

$$= -\frac{1}{V} \frac{\partial I}{\partial \beta}$$

Armed with this result for the two-particle interaction, we now return to the total potential energy $\bar{U}$:

$$\bar{U} \quad \frac{N^2}{2}\bar{u} = \frac{N^2}{2}\left(-\frac{1}{V}\frac{\partial I}{\partial \beta}\right) = -\frac{N^2}{2V} \cdot \frac{\partial I}{\partial \beta} \qquad (33.6)$$

Eq. (33.6) can be substituted into (33.4) to yield

$$\ln Z_U(\beta) = N \ln V - \left(-\frac{N^2}{2V}\right)\int_0^\beta \frac{\partial I(\beta')}{\partial \beta'} d\beta'$$

$$= N \ln V + \frac{N^2}{2V}\left[I(\beta) - I(0)\right]$$

However,

$$I(0) = \int (e^{-0} - 1) d^3 r = 0$$

so **FINALLY**

$$\ln Z_U(\beta) = N \ln V + \frac{N^2}{2V} I(\beta) . \qquad (33.7)$$

We've probably all got lost in the mathematics of obtaining this result, so let's state its importance: Eq. (33.7) tells us the leading order temperature dependence of the partition function away from the ideal gas partition function.

Non-ideal gas

Eq. (33.7) provides the correction terms to the ideal gas equation of state arising from interactions between particles in the dilute limit. To see its application, we calculate the pressure from

$$\beta \bar{p} = \frac{\partial}{\partial V} \ln Z$$

which becomes

$$\beta \bar{p} = \frac{\partial}{\partial V} \ln Z_U$$

because there is no other position-dependence than U in Z_{TOTAL}. Invoking Eq. (33.7),

$$\beta \bar{p} = \frac{\partial}{\partial V}\left[N \ln V + \frac{N^2}{2V} I(\beta)\right]$$

$$= \frac{N}{V} - \frac{N^2}{2V^{-2}} I(\beta)$$

$$= n - n^2\left[\frac{I(\beta)}{2}\right]$$

where n is the particle number density. This expression looks like the first two terms of the virial equation of state

$$\beta \bar{p} = n + B_2 n^2 + B_3 n^3 + ...$$

and leads to the identification

$$B_2 = -\frac{I(\beta)}{2} \qquad \text{or} \qquad B_2 = -\tfrac{1}{2}\int \left(e^{-\beta u} - 1\right) d^3 r \qquad (33.8)$$

for the second virial coefficient B_2.