Statistical Mechanics Notes for L. Susskind's Lecture Series, Part 6

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Abstract

This paper contains my notes on the sixth lecture of Leonard Susskind's 2013 Statistical Mechanics Stanford Lecture Series. (He also made a 2009 video series on the same topic.) They can be found on YouTube. Our goal in this paper is investigate one step beyond the ideal gas to a gas whose molecules are weakly interacting.

1 Getting Started

We begin with the system's energy.

$$E = \sum_n \frac{P^2}{2M} + \sum_{n>m} U(|\,\mathbf{x}_n - \mathbf{x}_m\,|)\,, \tag{1}$$

where $U(|\,\mathbf{x}_n - \mathbf{x}_m\,|)$ represents the interparticle interactions. However, the sum over the potential contributions will be approximated by an integral:

$$\sum_{n<m} U(|\,\mathbf{x}_n - \mathbf{x}_m\,|) \to \int d^3x_1 d^3x_2 U(|\,\mathbf{x}_1 - \mathbf{x}_2\,|)\,, \tag{2}$$

where $\mathbf{x}_1$ and $\mathbf{x}_1$ refer to two different points in the volume of interest. We shall perform this integration is two steps:

1) Hold one of the points fixed, and vary the other over all of space.

1) Hold the relative distance between the points fixed and integrate over all space as they move around. This procedure produces a factor that is the volume is the space of interest.

Step 1) $\int d^3XU(|\,x\,|) \equiv U_0$.

Step 2) This gives us a factor of VU_0:

$$\int d^3x_1 d^3x_2 U(|\,\mathbf{x}_1 - \mathbf{x}_2\,|) = VU_0 \tag{3}$$

From the energy expression we can calculate the partition function Z.

2 The Partition Function

$$Z = \int dp\,dx\,e^{-\beta P^2/2M} e^{-\beta U(x)} \tag{4}$$

where

$$\frac{P^2}{2m} = \sum_n \frac{p_n^2}{2M}\,, \tag{5}$$

and $U(X)$ stands for the potential energy as a function of all the positions. So,

$$Z = \int \frac{dp}{N!}\, e^{-\beta P^2/2M} \int dX \frac{e^{-\beta U(X)}}{V^n}\,. \tag{6}$$

The first integral on the RHS is the partition function for the ideal gas, $Z_0(\beta)$. In the second integral

$$\int \frac{dX}{V^n}\, e^{-\beta U(X)}\,, \tag{7}$$

$U(X)$ will be treated as the small parameter.

$$e^{-\beta U(X)} \approx 1 - \beta U(X)\,. \tag{8}$$

Hence, with $\int dX = V^N$:

$$\int \frac{dX}{V^n}\,[1 - \beta U(X) = 1 - \binom{N}{2} \int dX \frac{\beta U(X)}{V^n}\,. \tag{9}$$

The factor $\binom{N}{2}$ relieves us of the necessity of having to sum on both particles.

Now,

$$\binom{N}{2} \approx N^2\,, \tag{10}$$

hence

$$1 - \frac{\beta N^2}{2} \frac{V^{n-2}}{V^n} V U_0 = 1 - \frac{\beta N^2}{2} \frac{U_0}{V}\,. \tag{11}$$

Therefore,

$$Z = Z_0(\beta)\Big[1 - \frac{\beta N^2}{2V} U_0\Big]\,. \tag{12}$$

So,

$$\log Z = \log Z_0 + \log\Big[1 - \frac{\beta N^2}{2V} U_0\Big]\,. \tag{13}$$

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3 Energy and Pressure

$$\begin{aligned}
\bar{E} &= -\frac{\partial \log Z}{\beta} = N\tfrac{3}{2}T + \frac{N^2}{2V}U_0 \\
&= \tfrac{3}{2}NT + \tfrac{1}{2}N\rho U_0 \\
&= \big[\tfrac{3}{2}T + \frac{\rho}{2}U_0\big]N\,.
\end{aligned} \tag{14}$$

Now,

$$A = -T \log Z\,, \tag{15}$$

and, from Part 5 of this series, page 3, Eq. (21):

$$
\begin{aligned}
P &= \frac{\partial A}{\partial V}\Big|_T = T\frac{\partial \log Z}{\partial V} \\
&= \frac{NT}{V} + \beta T \frac{\partial \log Z_0}{\partial V}\Big|_T \\
&= \frac{NT}{V} + \beta T \frac{N^2}{2V} U_0 \,.
\end{aligned} \tag{16}
$$

With $\rho = N/V$, therefore,

$$
P = \rho T + \tfrac{1}{2}\rho^2 U_0 \,. \tag{17}
$$

Now, imagine a gas contained in a cylinder-piston arrangement. Imagine the piston moving in or out slowing, allowing no chance for heat exchange with the environment. Then,

$$
\bar{E} = -PdV \,. \tag{18}
$$

Remember, that, holding the volume fixed, we have that

$$
\bar{E} = TdS \,. \tag{19}
$$

Combining these last two equations yields,

$$
\bar{E} = -PdV + TdS = dW + dQ \,, \tag{20}
$$

where dW is the work done by the piston on the gas, and dQ is the heat exchanged. Equation (20) is the First Law of Thermodynamics.