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SIF40AH/DIF4997
Nano-particle and polymer physics I
SOLUTION of EXERCISE 5

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*Eq. (x.x) refers to version AM11sep02 of lecture notes: "Nano-particle and polymer physics".
Equations pertinent to this exercise you will find in Appendix B and Ch. 4.4.*

A) When gravitational effects are not included, the list of variables being candidates to the problem is:

Variable	Symbol	Dimension
Pressure	p	Nm^{-2}
Particle size	r	m
No. of polymers per volume	ρ_N	m^{-3}
Cylinder diameter	d	m
Temperature	T	K
Boltzmann's constant	k_B	NmK^{-1}

The Hooke's constant of the polymer is included in the size r (see comments at the end of solution). Thus there are $N^{(P)} = 6$ parameters and $N^{(D)} = 3$ actual dimensions (newton, meter and kelvin).

B) The temperature can be included only in the combination $k_\text{B}T$, as kelvin appears in T and k_B only and this is the only possible dimensionless combination where K disappears. Then we have $N^{(P)} = 5$ parameters and $N^{(D)} = 2$ actual dimensions. Thus we can construct $N^{(P)} - N^{(D)} = 3$ dimensionless variables. We obtain the following dimension matrix.

	p	r	ρ_N	d	$k_\text{B}T$
N	1	0	0	0	1
m	-2	1	-3	1	1

As the core variables we choose d and $k_\text{B}T$. This is permitted since the co-determinant $\begin{vmatrix} 0 & 1 \\ 1 & 1 \end{vmatrix} = -$

of these variables is not zero. That is, we find the dimensionless variables π_i:

$$\pi_1 = \frac{p}{k_\text{B}Td^{-3}} = \frac{p}{k_\text{B}T}d^3 \tag{1}$$

$$\pi_2 = \frac{r}{d} \tag{2}$$

$$\pi_3 = \frac{\rho_N}{d^{-3}} = \rho_N d^3 \tag{3}$$

E.g. π_1 is found by setting $\pi_1 = \dfrac{p}{(k_\text{B}T)^\alpha d^\beta}$ and determine α and β from the dimension matrix.

C) According to Pi-theorem the relation $p = p(r, \rho_N, k_\text{B}T, d)$ can equivalently be replaced by

$$\pi_1 = \Psi(\pi_2, \pi_3)$$

$$\text{or:} \quad \underline{p} = \underline{\frac{k_\text{B}T}{d^3} \cdot \Psi(\frac{r}{d}, \rho_N d^3)} \tag{4}$$

D) Without any physical knowledge we can not come any further. However, to gain explicit results (and illustrate the technique) we will now inspect som special cases where we are able to deduce the function $\Psi()$.

i) Assume there are no interaction between the polymers. Then it is expected that the pressure must be proportional to the number of polymers per volume: $p \propto \rho_N$. In dimensionless variables

this means that π_3 is separable from Ψ:

$$\Psi(\pi_2, \pi_3) = \pi_3 \cdot \Phi(\pi_2)$$

From Eq. (4) and (3) we obtain the pressure

$$p = \rho_N \cdot k_B T \cdot \Phi(r/d) \tag{5}$$

ii) Further, in order to have finite pressure in the limit of very small polymers, $r/d \to 0$, we must require

$$\lim_{r/d \to 0} \Phi(r/d) = \text{constant}.$$

And we know from the the ideal gas law that the constant equals unity:

$$p = \rho_N k_B T, \tag{6}$$

as it should, because the polymers now are small, hard spheres without interaction.

iii) In the limit of very large polymers, $r/d \to \infty$, we define $\Phi(r/d) \propto (r/d)^\gamma$ and search to determine the exponent γ. The pressure is given by $p = -\frac{\partial A}{\partial V}$, where A is the Helmholtz free energy $A = U - TS$, and $U = 0$ when we assume the polymers to be pure entropy springs. (The pressure mainly origin from the deformation of the polymer chain.) The entropy is linear in the polymer number N, thus also A, $\frac{\partial A}{\partial V}$ and p are linear in N. But how enters the polymer size r? Yes, we know that for chain molecules in any models $r^2 \propto Na^2$, where a is a typical monomer size. To obtain p linear in N, the pressure must thus be quadratic in r and thus $\gamma = 2$. Conclusion:

$$p = \rho_N k_B T \cdot \frac{r^2}{d^2} = \rho_N k_B T \cdot \frac{Na^2}{d^2}. \tag{7}$$

E) Comments:

i) We compare Eq. (6) and Eq. (7) with the respective equations in lecture notes, Eq. (4.64) and (4.67) when a polymer is restriced to a (three-dimensional) box. In the lecture notes one polymer is used, which means that $\rho_N d^3 = 1 \Rightarrow \rho_N = d^{-3} \propto 1/V$. We find that Eq. (6) equals Eq. (4.64). Accordingly we can in Eq. (7) use that the polymer size is given by $r^2 = Na^2 \propto Nk_B T/H$, H being Hooks's constant. Full consistence.

ii) What about including Hooke's constant H explicitly from the very beginning? This would have been natural if we consider the expressions for pressure in lecture notes. Then we must include one more dimensionless parameter, $\pi_4 = \frac{Hd^2}{k_B T}$. Eq. (6) then would read $p = \rho_N \cdot k_B T \cdot \Phi\left(\frac{Hd^2}{k_B T}\right)$, and we can argument that $\Phi = \text{constant}$ because p should be independent of H in this limit. Therefore Ψ is independent of π_4 and we have returned to our original setup. A similar argument could be applied for not including N.

iii) Note that we chose the length d as the primary variable and not r. This is because we wanted to express p as function of r.