

Swapan Kole[†]

Average Quantities

This has reference to the article “Average Quantities – Molar Mass of Polymers and Molecular Speed in Fluids” published in ISC in July 2021. As regards the motivation behind and the analysis of the article, I have something to point out.

A gas at equilibrium assumes Maxwellian distribution for molecular speed. Calculations reveal that the root mean square (rms) speed c for such systems is related to mean speed $\langle c \rangle$ through the relation $c \approx 1.0854 \langle c \rangle$. However, it is not a general proof for the inequality $c > \langle c \rangle$.

In many important situations, the speed distribution of the constituent particles of a system is non-Maxwellian. For example, the speed values of the molecules of a monatomic gas at any instant in a very strong magnetic field follows a non-Maxwellian distribution function owing to the electrical polarization and its saturation for the atoms. In Coulombic systems, such as plasma state of matter and the charged particles in the solar wind as well, the speed distribution of the particles is essentially non-Maxwellian. It encouraged to opt for a general system to show that $c > \langle c \rangle$. An arbitrary system was treated rigorously to obtain the results successfully.

Further, I would like to point out that the desired goal, namely to show $c > \langle c \rangle$, could be achieved easily if we had applied statistical methods. I shall discuss it now. We have the relations :

$$\langle c \rangle = \frac{1}{N} (v_1 + v_2 + \dots + v_N)$$

$$c^2 = \frac{1}{N} (v_1^2 + v_2^2 + \dots + v_N^2)$$

The variance (σ^2) in the molecular speeds (where v_1, v_2, \dots, v_N are the molecular speeds) can be expressed as

$$\sigma^2 = (v_1 - \langle c \rangle)^2 + (v_2 - \langle c \rangle)^2 + \dots + (v_N - \langle c \rangle)^2$$

= a positive quantity.

By using standard methods, it can also be shown that : $\sigma^2 = c^2 - \langle c \rangle^2$

Hence we obtain that $c^2 > \langle c \rangle^2$ or $c > \langle c \rangle$ because both c and $\langle c \rangle$ are positive numbers.

Next we concentrate on different types of molar masses of a polymer sample. Usually, the number- and weight-average molar masses ($\langle M_n \rangle$ and $\langle M_w \rangle$) of a polymer sample are related by the equation, $\langle M_w \rangle = 2 \langle M_n \rangle$, which satisfies the inequality $\langle M_w \rangle > \langle M_n \rangle$. However, this is not a general proof, because the above equation was developed for “most probable distribution”, which occurs in step-growth or condensation polymerization. Another important distribution, the Poisson distribution is observed in anionic polymerization where initiation is too fast compared to propagation, and usual termination of the polymerization process is absent, which creates realities and terminologies like ‘living polymers’ and ‘living polymerization’. In addition, there are various ways of controlling molecular size and size-distribution. Thus an arbitrary distribution was chosen to represent any of these polydispersed systems, and treated rigorously to show that $\langle M_w \rangle > \langle M_n \rangle$ in the said previous article. However, these systems could not be fitted to the available statistical models for an easier solution, which justifies the elaborate analysis adopted in the above-mentioned article.

[†]AKPC College, Bengai, Dist. Hooghly, West Bengal

ORCID: Swapan Kole: <http://orcid.org/0000-0002-9436-2744>