Approximation of viscosity average molecular weight of polyethlene glycol

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The viscosity average molecular weight of polyethelene glycol is approximated using Mark-Houwink's empirical equation, and intrinsic viscosity is obtained using Huggins' equation and Kramer's equation respectively. The reliablity of thermostat is investigated in detail, exploring several factors that affect the fluctuation of the temperature. Programs are also utilized to reveal some basic relation between these factors, as well as indicating some plausible improvements for further stabilization of the temperature.

Keywords: viscosity average molecular weight, polyethelene glycol, thermostat

CONTENTS

I. THE FLUCTUATION OF TEMPERATURE IN THERMOSTAT

The fluctuation of temperature is a key factor in measuring viscosity of liquids, whose huge dependence on temperature greatly affects whether a strong linear relation between viscosity and density can be obtained. The characteristics of the fluctuation curves are investigated in detail using computational methods.

A. Simulations

Heat flow satisfies

$$\frac{d\mathbf{q}}{dt} = -D_f \nabla T, \tag{1}$$

while the temperature at a point also satisfies

$$\frac{dT}{dt} = C_V \iint \mathbf{q} \cdot d\sigma. \tag{2}$$

In one-dimension discrete model, the equations reduce to

$$\begin{cases} \frac{\Delta q}{\Delta t} \sim D_f \frac{T(x+\Delta x)+T(x-\Delta x)-2T(x)}{2\Delta x} \\ \Delta T(x) \sim \frac{\Delta q/\Delta t}{C_V} \Delta t \end{cases} \tag{3}$$

The exact model set up using *Julia* includes a linearly heated cell, a cell whose temperature is fixed to the room temperature, and a temperature measuring cell which controls heating through comparing its temperature measured to the target temperature set initially.

$$\begin{cases} \Delta T/\Delta t|_{\text{heat cell}} = k \\ T(\text{wall}) = T_{\text{room}} \end{cases} \tag{4}$$

Specifically, the model adopts 30 cells and Δt is set to 0.01 s[1], and all the simulations go through 100,000 iterations.

The relation between fluctuation and heating speed is investigated, whose result is shown in Fig.1, where a sharp increase can be observed at initial stage. This can easily be attributed to the 'delay' of measurement of temperature, derived from the time inquired for the heat flow to 'pass over' the measuring cell. A non-sinusoidal behavior is also revealed,

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which results from the unequality between heating speed and cooling speed. At temperature relatively close to the room temperature results in lower speed of cooling, which leads to more time spent in reducing the exceeded temperature. Fig.2 further explains this result, introducing the fact that the fluctuation become sinusoidal as the target temperature increases. Fig.1 also indicates higher frequency,smaller amplitude of the fluctuation and less to time spent to achieve such a state, when lower speed of heating is set.

Fig.2 further shows a slight difference of frequency and amplitude among different target temperature, which is also derived from the different speed of cooling. The same reason can be applied to the facts that the mean of the temperature is universally higher than the target temerature, and that the mean temperature gradually approaches the target temperature when it increases.

Fig.3 helps draw the conclusion that smaller distance between heat source and temperature measuring device

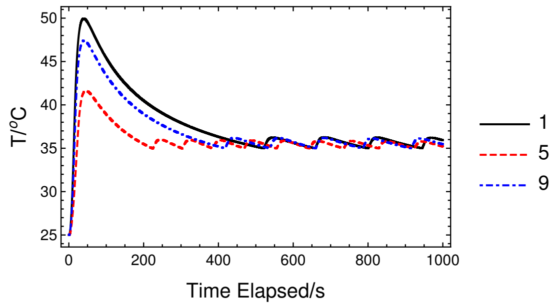

FIG. 1. The flctuation curves having heating speed as the main variant. The numbers in legends shown represent the heating speed in the simulations.

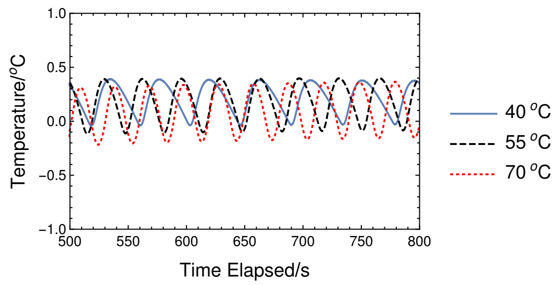

FIG. 2. The flctuation curves having target temperature as the main variant. The y-axis represents the deviation from the target temperature.

leads to better stability of temperature around the measuring device. From another perspective, the trend of the curve in the cell away from both the heat source and the measuring cell differs from cells between them, namely that rather than fluctuating it shows a converging behavior towards target temperature. This might indicate a better position in thermostats for thermo-sensitive experiments.

Dual heat sources might not be appropriate for stabilizing the temperature in thermostats, as shown in Fig.4. Even equating the power of the heat source does not restrict the amplitude of fluctuation. Lower frequency

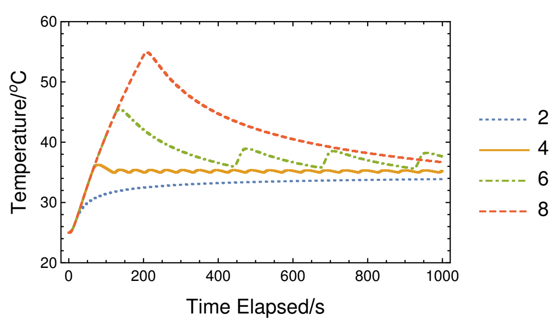

FIG. 3. The flctuation curves having the position of the measuring cell as the main variant, concerning temperature of the third cell. The numbers in legends represent the index of the measuring cell in the array.

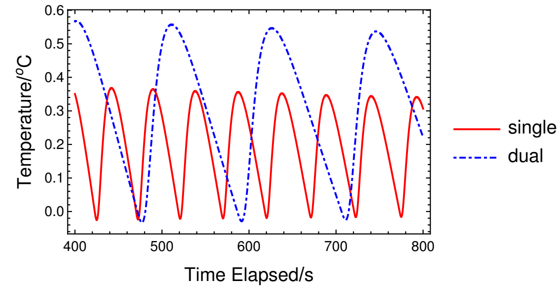

FIG. 4. The flctuation curves concerning whether there is single heat source or dual. The other heat source is set at 7^{th} cell and the heating speed of both heat sources is set half of it in single-heat-source model.

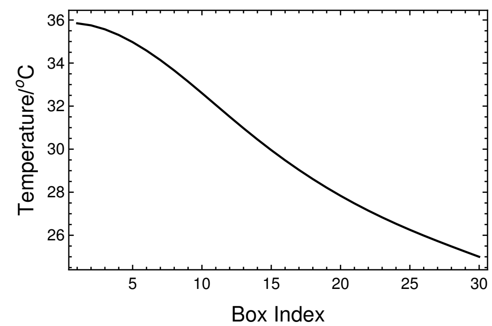

FIG. 5. A snapshot from the dual-heat-source model

might also results in worse experimental conditions. A snapshot from the dual-heat-source model shown in Fig.5 denies the mind-set that a relatively mild decrease can be obtained between the two heat sources, which might results from quicker heat flow and then easier excess of heat supply.

B. Experimental Results

Fig.6 presents the heating process, most characteristics of which have been indicated by numerical simulations, including an excess of temperature before fluctuation, as well as non-sinusoidal behavior. The asymmetry of the fluctuation curve remsembles the one provided in simulations, which further validates the computational model. Fig.7 also reveals the relation between heating speed and the fluctuation's amplitude and frequency, which is the same as deduced in simulations. Smaller amplitude and higher frequency in experiments are attributed to better thermal conduct than in simulations.

0.04 °C of deviation in thermostat under 110 V indicates that the following experiment, namely the measurement of viscosity of polymer's solution and approxmation of polymer's molecular weight, is executed under relatively stable thermal conditions.

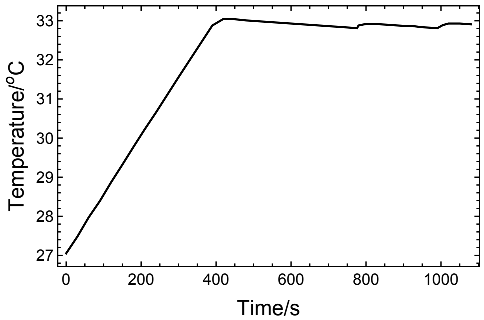

FIG. 6. Heating of water with heater under voltage of 220 V and target temperature set at 32 °C

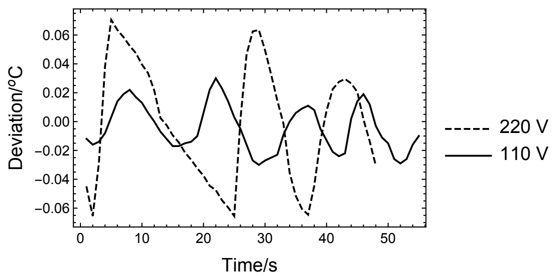

FIG. 7. Fluctuation of temperature under heating voltage of 220 V and 110 V

II. THE MEASUREMENT OF VISCOSITY OF POLYMER'S SOLUTION, AND APPROXMATION OF POLYMER'S MOLECULAR WEIGHT

The temperature of the thermostat is set to 35 °Cin the experiment, and the fluctuation has been proved to be trivial. Table.I and Table.II contain the experimental results, and Table.III concludes the $[\eta]$ calculated from two groups and two methods. The density of polyethylene glycol solution adopts 'unit' as its unit proportional to standard unit, causing no confusion nor error in the approximation of $[\eta]$. Fig.8 shows the linear fitting of the data. It is defined that

$$\begin{cases} [\eta]' = \frac{\eta_{\mathrm{sp}}}{c} \\ [\eta]' = \frac{\eta_{\mathrm{r}}}{c} \end{cases}$$

Group A and group B differs from each other due to different pipes used in the experiment[2]. Different results of $[\eta]$ indicates a strong connection between η and the pipes, which seems reasonable with regard to the fact that polyethelene glycol can form strong hydrogen bonds

TABLE I. Group A

density/unit	t/s	η_{r}	η_{sp}
0.	80.48	1.000	0.000
1.	89.94	1.118	0.118
2.	100.7	1.252	0.252

TABLE II. Group B

density/unit	t/s	η_{r}	η_{sp}
0.	71.12	1.000	0.000
3.	99.43	1.398	0.398
4.	110.7	1.557	0.557
5.	121.5	1.709	0.709

TABLE III. $[\eta]$ obtained from two groups, two methods

	Group A	Group B
$\frac{\eta_{\mathrm{sp}}}{c}$	0.109	0.120
$\frac{\ln \eta_{\mathrm{r}}}{c}$	0.110	0.119

with SiO_2, which is the main substance of the glass pipe. Different pipes are certain to have different surfaces, and η of the solution may thus differ significantly. Two methods calculating $[eta]$ return nearly the same results in each group, validating the data of the experiment.

Data from Group A gives 14.5×10^4 as the polyethelene glycol's viscosity average molecular weight, while it is 16.2×10^4 from Group B.

III. ACKNOWLEDGEMENTS

Special thanks must be given to Zong Wei Huang, who dedicated himself in achieving computational approximation of viscosity of polymer solutions yet did not hesitate to provide enormous help for the realizeation of program and analyses of the results. His work adopting Monte Carlo is certainly impressive, citation of which fais to be included in this report due to limitation of time.

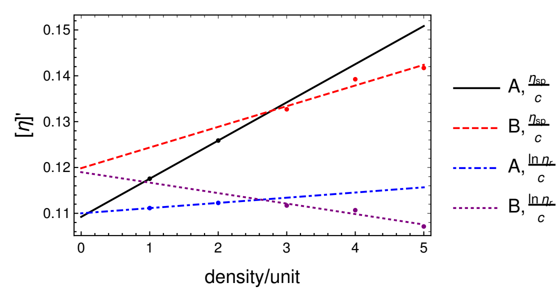

FIG. 8. $[\eta]'$-c curves for two groups, two methods

[1] The model is relatively sensitive to the value of Δt, which mainly determines the numerical unstability of the whole simulation, namely the fluctuation of the data itself.

[2] It is due to unintentional crack observed in the pipe first used, while limitation of time hinders completion of data.