Theoretical analysis of thermo-responsive behavior of microgels loaded with silver nanoparticles

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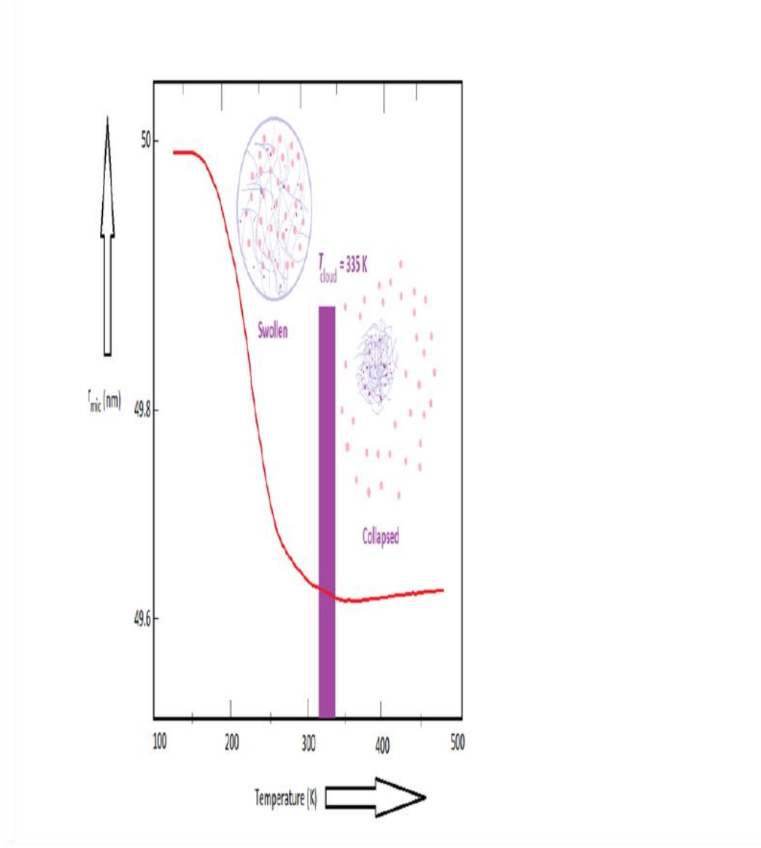
Abstract



Temperature is one of the extremely significant factors responsible for modifications mostly in physical but also chemical properties of some particular matter. In the present study, we theoretically analyzed the thermo-responsive behavior of Ag-p (N-isopropylmethacrylamide) hybrid microgels. We employed the classical Maxwellian distribution function concerning the velocity of spherical silver nanoparticles inside the microgel's network. The behavior of the distribution function relative to the temperature represents that the distribution function still obeys the Maxwell-Boltzmann law even at low temperatures. Further, the diffusion coefficient, probability density, surface tension, and surface energy of silver nano-particles are numerically evaluated and then graphically illustrated.

1. Introduction

The properties of silver nanoparticles applicable to human treatments are under investigation in laboratory and animal studies. These properties are used for assessing potential efficiency, bio-safety and bio-distribution. Various shapes of nano-particles can be constructed depending on the application at hand. Commonly used silver nanoparticles are spherical.

Soft, spherical and porous materials that can exhibit rapid response to several exterior environmental stimuli like temperature [1], pH [2], magnetic field [3], glucose concentration [4], light [5], and enzymes [6] are termed as smart microgels. Construction of N-isopropylacrylamide (NipAam) or N-isopropylmethacrylamide (NipMam) based microgels results the formation of thermo-responsive microgels [7]. Their thermo-responsive behavior is attributed to some sort of variation in inter/intra-molecular forces, constructing their structure as a joint network, in response to increase or decrease in temperature.. The most studied thermo-responsive microgels are constructed by N-alkylacrylamide family and more specifically NipAam.

Usually microgels are synthesized by precipitation polymerization process. The ingredients involved are main monomer NIPMAM, a co-monomer methacrylic acid MAA, Crosslinker Methylene bis acrylamide (BIS), a surfactant and initiator.. Precipitation polymerization is carried out at a temperature greater than VPTT of main monomer i.e; NIPMAM, 70 °C in usual practice. Surfactant aims to take the mono-dispersity in size of microgel particles. A lot of work in synthesis, characterization and applications is already done..

Now, there is a need to extend this excellent system towards physics. There are very large number of aspects required to be addressed. We are here to deal with the ease of mobility, i.e.; the diffusion coefficients of organic microgels and inorganic nanoparticles together in the same framework. On employing the classical Maxwellian distribution function with respect to the velocity of spherical silver nanoparticles inside the microgel's network, the behavior of distribution function with respect to the temperature is studied. It represents that the distribution function still obeys the Maxwell–Boltzmann law even at low temperatures [8]. Further, the probability density of silver nanoparticles within the voids of microgel particles and the surface tension of microgels in aqueous medium are also discussed in detail. Moreover, to the best of our knowledge we are pioneers to address this physico-chemical aspect of microgel particles.

2. Formalism

2.1. Numerical analysis

The main focus of our numerical analysis is based on an important parameter i.e., temperature, which can change a few chemical but complete physical properties of some particular matter. Firstly, the diffusion of microgel particles with respect to the temperature is evaluated as

$$D^T = \frac{k_B T}{6\pi\eta r_{mic}} \qquad \text{---------------(1)}$$

Table 1
Temperature effect on diffusion coefficient.

$T(K)$	298	315	335	372
D_T (cm^2 s^{-1}) $\times 10^{-9}$	0.99	1.05	1.12	1.24

It shows that the increase in temperature causes the increase in diffusion of hybrid microgel.

Now, we discuss the effects of temperature on the probability density of spherical silver nanoparticles after evaluating it within the microgel. These silver nanoparticles can be positive, neutral or may be negatively charged.

This distribution function will be classical Maxwellian in the presence of thermal temperature i.e.,

$$\begin{aligned} f(v) &= 4\pi\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} v^2 \exp\left[-\frac{mv^2}{2k_B T}\right] \\ &= Av^2 \exp\left[-\frac{mv^2}{2k_B T}\right] \end{aligned} \qquad \text{--------(2)}$$

Where A is the normalization constant for any specific temperature and k_B=1.3807 × 10^{-16} $cm^2\ g\ s^{-2}K^{-1}$ is the Boltzmann constant.. In the following, the Table 2 represents the decrease in values of temperature dependent normalization constant with the increase in possible low temperatures for our given system.

Table 2
Temperature effect on normalization constant.

$T(K)$	298	335	372
$A \times 10^{-9}$	54.9	46.1	39.4

The velocity range is must be $0 \le v < \infty$ for non-relativistic particles. Therefore, we get

$$\int_0^b f(v)dv = A\Gamma\left[0, \frac{m_{sn}}{2k_B T b}\right] \qquad \text{-------(3)}$$

The upper limit b of spherical silver nanoparticles i.e., the most probable speed $c_{mp} = \sqrt{\frac{2k_bT}{m_{sn}}}$ and thus the probability density of the particles can be evaluated at three different values of temperature .

Table 3
Temperature effect on most probable velocity and probability density.

T(K)	298	335	372
c_{mp}(cm s^{-1})	345	366	386
$\int_0^b f(v)dv \times 10^{-7}$	9.31	7.90	6.81

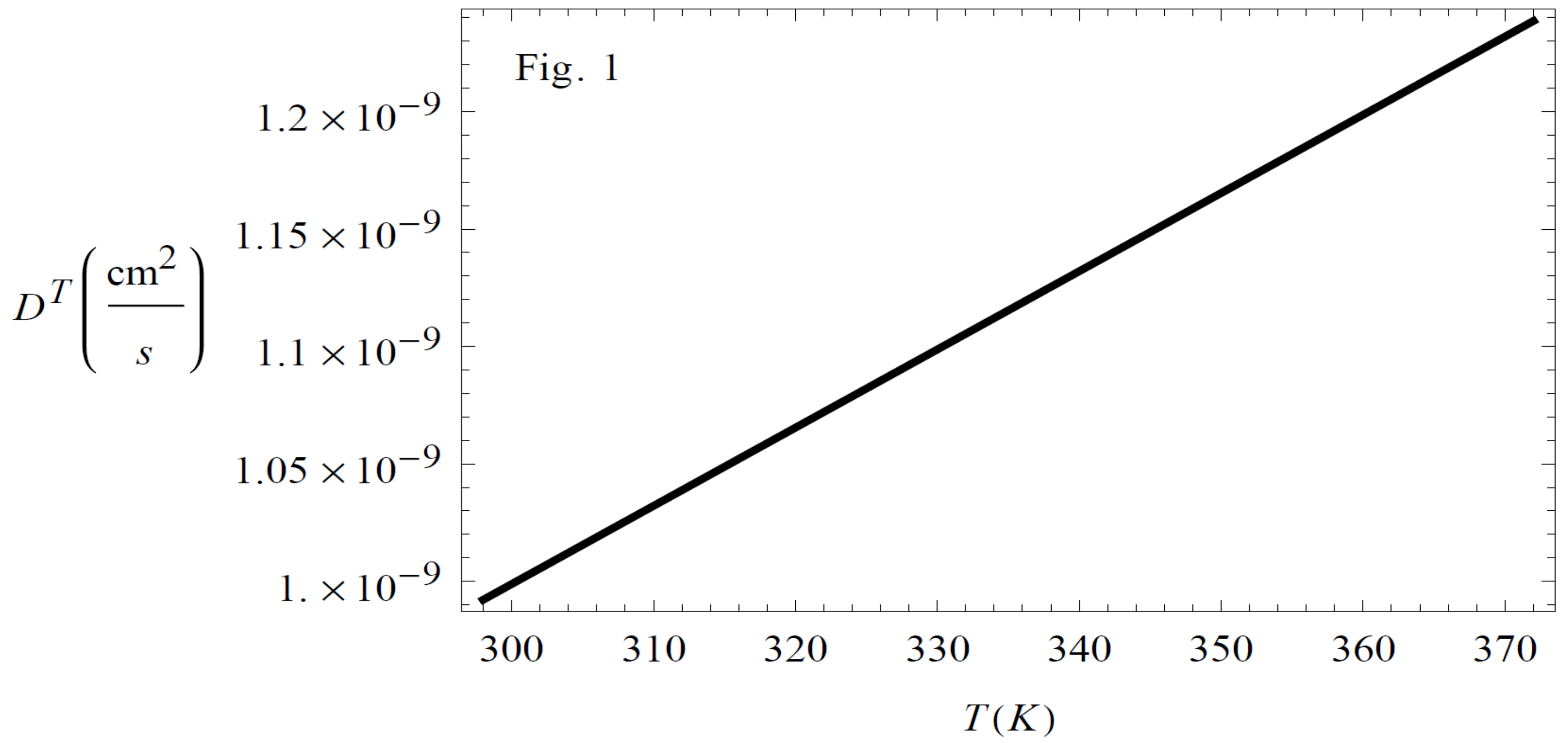
Thus most of the spherical nanoparticles move out from microgel and microgel shrinks, at that time the mass of 3 mL hybrid microgel is observed as m_{mic}=2.932 g. The area and volume of spherical microgel particles are evaluated as $A_{mic} = 3.14 \times 10^{-10}\ cm^2$ and $V_{mic} = 5.23 \times\ 10^{-16}\ cm^3$, where radius $r_{mic} = 50 \times 10^{-7}\ cm$ and density $\rho_{mic} = 0.56 \times 10^{16}\ g\ cm^{-3}$. Similarly, for spherical silver nanoparticles we have considered mass m_{sn}=6.91× 10^{-19} g, area $A_{an} = 3.14 \times 10^{-12}\ cm^2$ and $V_{sn} = 5.23 \times\ 10^{-19}\ cm^3$, where radius $r_{sn} = 5 \times 10^{-7}\ cm$ and density $\rho_{sn} = 1.32\ g\ cm^{-3}$. Now we examine the effect of temperature on surface area per unit volume or surface area per unit mass of both spherical microgel as well as nano-particles and further compare their results. It is noticed that whether we talk about area per unit volume or area per unit mass the surface area of large microgel particles will be very small as compare to the small nano-particles but with the increase in temperature when microgel particle's size will be reduced then it's surface area per unit volume or mass will be increased. Due to the large mass and size of spherical microgel particles the effect of mass directly related to the concentration of particles is the most prominent feature in order to enhance the surface tension because it causes a great increase in intermolecular forces between the particles of microgel. Moreover, it is the concentration of particles which can also reduce or control the effect of temperature on particle's distribution.
Now to study the elastic properties of microgel one can numerically estimate the values of squeezing microgel's radius (from Eq. (1)) with respect to the increase in temperature, employing the evaluated values of diffusion coefficient relevant to the temperature as mentioned in Table 1.

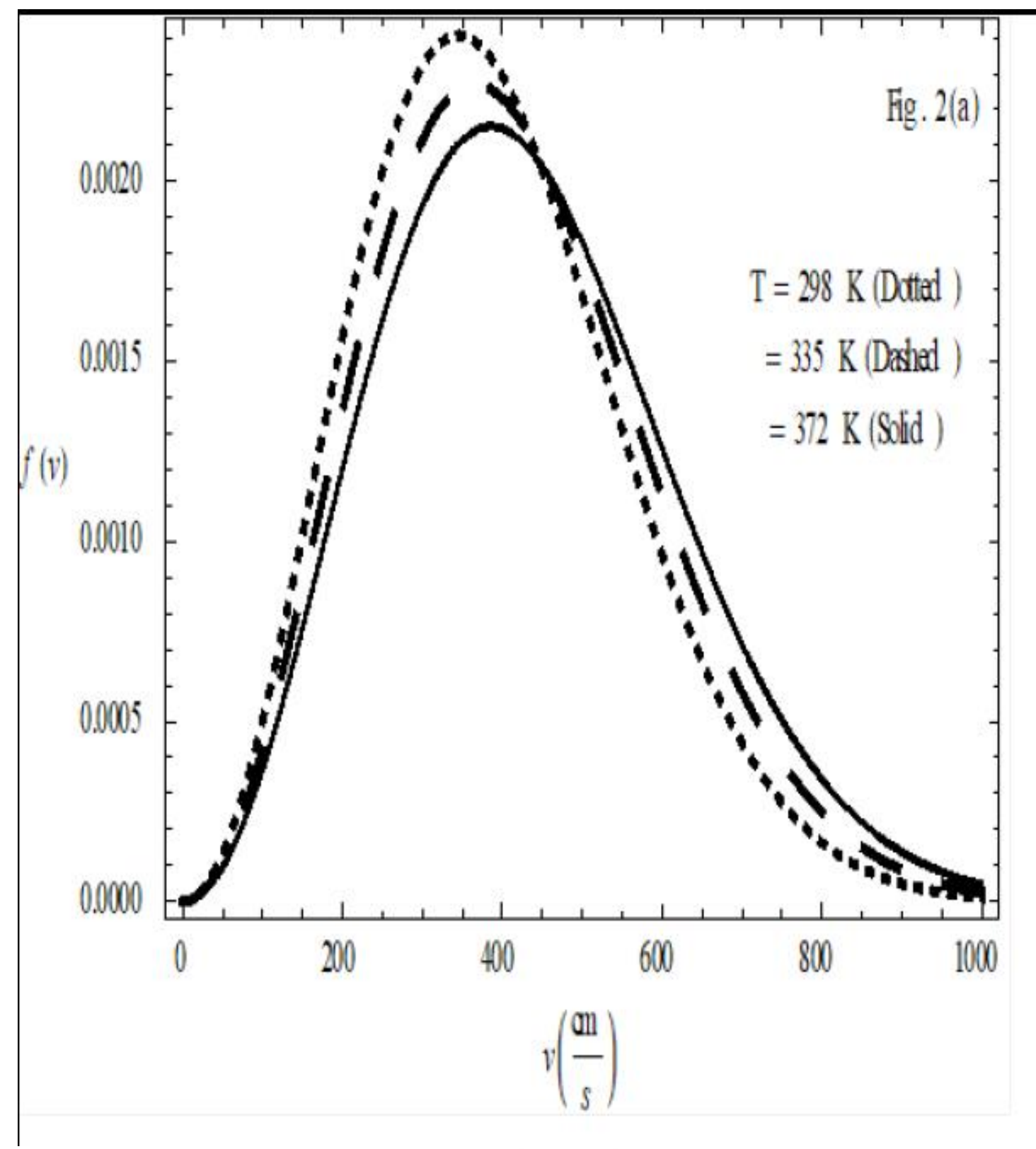
Table 4
Temperature effect on size of microgel.

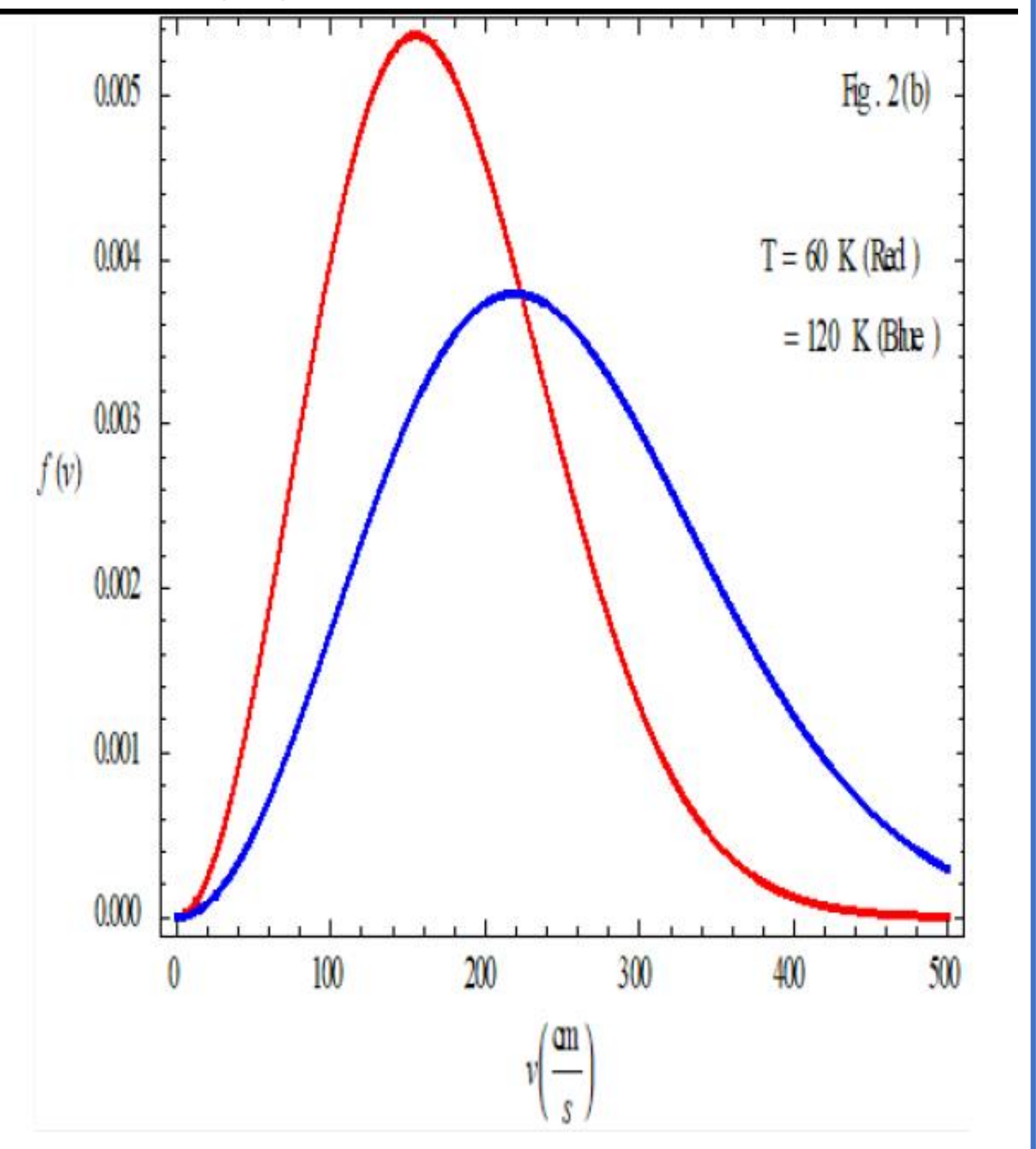
T(K)	298	315	335
r_{mic}(nm)	50	49.96	49.82

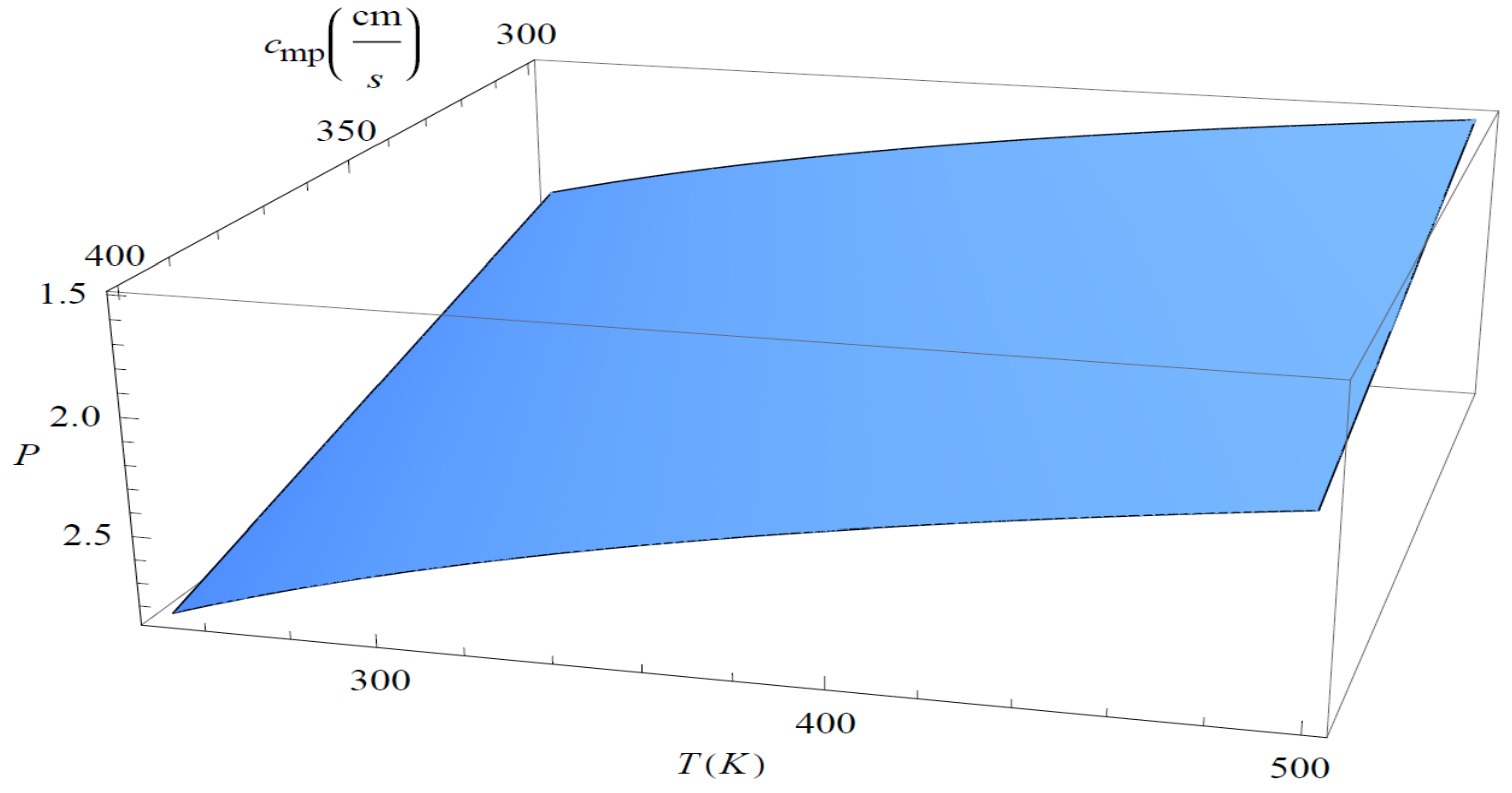
As elasticity is the ratio of stress to strain hence the microgel has maximum elasticity at T = 298 K. Therefore, elasticity has inverse relation with temperature such as the size of microgel decreases due to the increase in temperature. This increase in temperature reduces elasticity and causes the microgel to become more stiff.

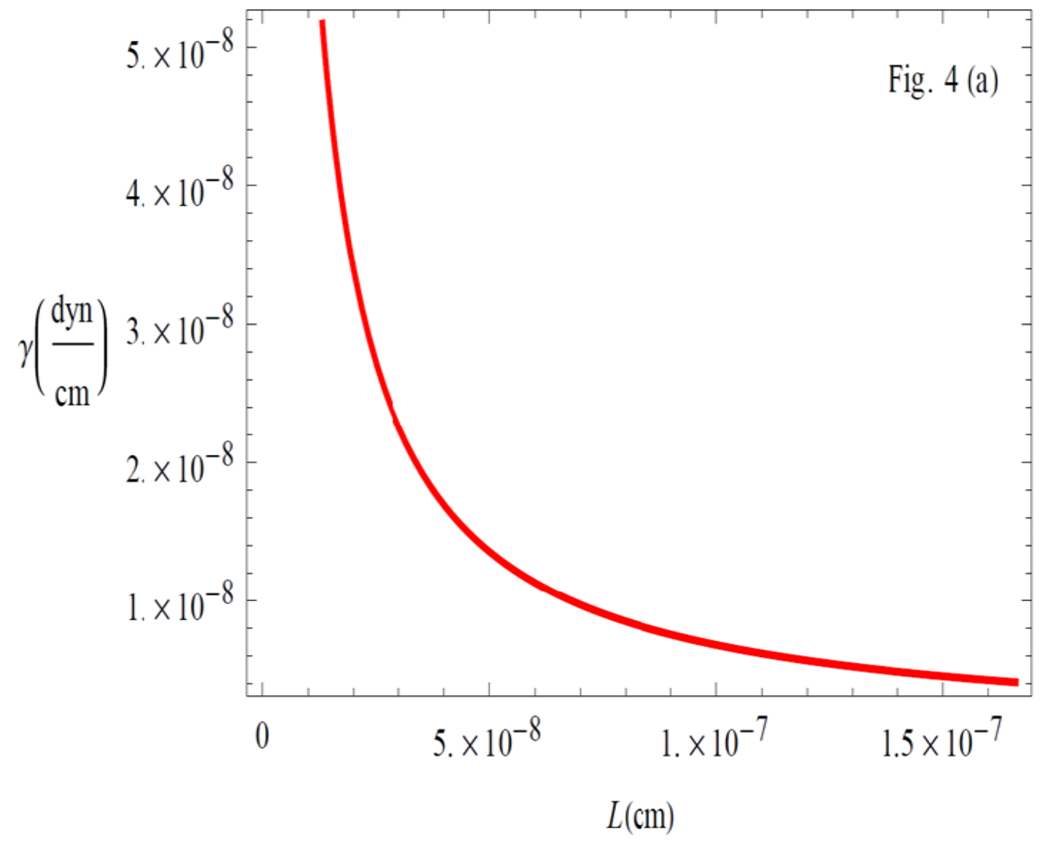
3. Graphical Analysis

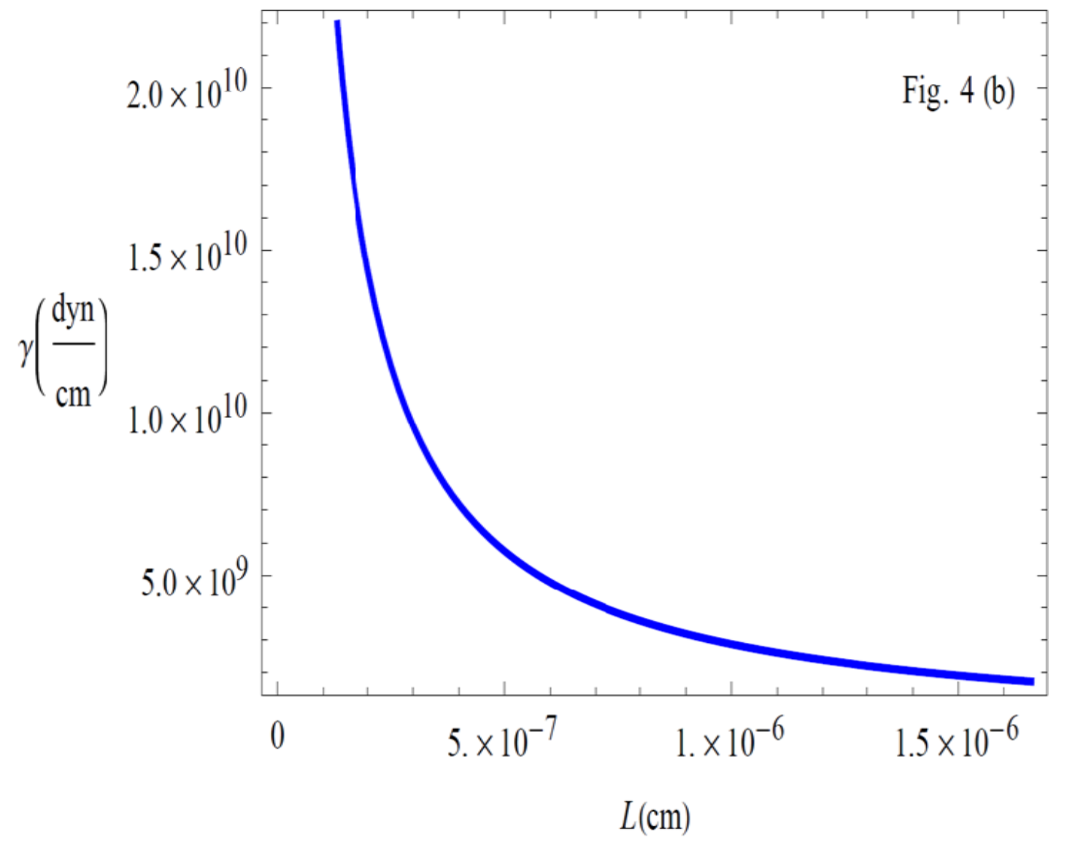


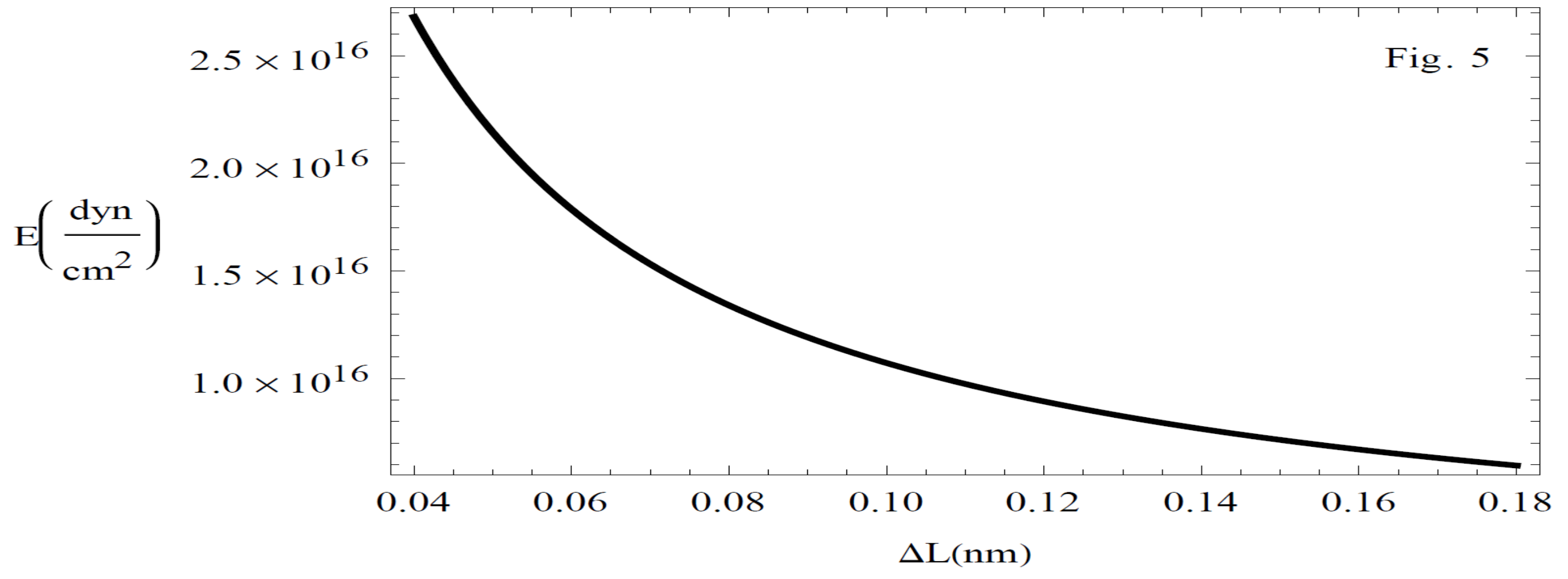












4. Discussion and Conclusions

we have discussed the effect of temperature on both microgel as well as on silver nano-particles. The increase in temperature causes the increase in diffusion, the velocity and hence the kinetic energy of the particles. However, it decreases the temperature dependent normalization constant (A) as well as the probability density (P) of the particle. In case of microgel which was initially in swollen state the distribution of particles increases with temperature until a critical temperature is reached for volume-phase transition. After that critical temperature, the microgel starts shrinking which reduces the size of microgel and hence the distribution of particles inside it. Further, the results represent that the surface tension is greater for the greater particle concentration and the particle size. However, the effect of particle concentration is the most prominent feature over particle's size. This is because the Van der Waals force between the particles at liquid interface increases the surface free energy and the surface tension.

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