

AN EXACT ENUMERATION STUDY ON ADSORPTION TRANSITION OF A TETHERED CHAIN AT AN ADSORBING SURFACE*

Wen-qin Lu** and Meng-bo Luo

Department of Physics, Zhejiang University, Hangzhou 310027, China

Abstract The number of configurations, $c(n, m)$, of a single chain with length n attached to a flat surface with m monomers contacting the surface is exactly enumerated. A function of $c(n, m)$ about m and n is obtained. From the function, a scaling law for mean energy of chain is derived, and we estimate the critical point $\varepsilon_c = 0.276$ and the crossover exponent $\phi = 0.5$. The free energy difference between tethered chain and free chain in dilute solution is also studied, which shows the critical adsorption point is about 0.272 for infinite long chain with $\phi = 0.5$.

Keywords: Critical point; Exact enumeration; Adsorption transition; Polymer chain.

INTRODUCTION

When a tethered polymer molecule in dilute solutions of good solvents interacts with a flat surface, it may undergo an “adsorption transition”^[1–5] from a three-dimensional configuration for a weakly attractive or repulsive interaction to a quasi-two-dimensional configuration for a strongly attractive interaction. The adsorption of polymers on attractive surfaces is relevant to many technological applications and biological processes, and it has attracted extensive studies from both experimental and theoretical aspects. The theoretical treatment of the adsorption of polymer molecules on an attractive surface within the framework of statistical mechanics has been a long standing problem^[6–9] that still gains a lot of interests^[10–16].

A mathematical model often used for studying polymer adsorption on surfaces is the self-avoiding walk (SAW) chain in a three-dimensional lattice interacting with a flat surface and restricted to lie on one side of the surface. Every walk contacting with the surface is assigned an interacting energy $-\varepsilon$. For simplicity, $k_B T$ is used as the energy unit composed of the Boltzmann constant k_B and temperature T . The chain exhibits a phase transition at a critical adsorption energy, $-\varepsilon_c$, from a desorbed state at $\varepsilon < \varepsilon_c$ to an adsorbed state at $\varepsilon > \varepsilon_c$. The value ε_c is named as the critical adsorption point (CAP). Whittington^[7] obtained bounds of the limit of free energy for an adsorbed chain with infinite chain length n . Hammersley *et al.*^[2] proved that the limit of free energy, $F(\varepsilon) = \lim_{n \rightarrow \infty} \frac{1}{n} \ln Z_n(\varepsilon)$, exists and ε_c can be defined by

$$\begin{cases} F(\varepsilon) = \ln \mu_d & \text{if } \varepsilon \leq \varepsilon_c \\ F(\varepsilon) > \ln \mu_d & \text{if } \varepsilon > \varepsilon_c \end{cases} \quad (1)$$

where $Z_n(\varepsilon) = \sum_{m=0}^n c(n, m) e^{m\varepsilon}$ is the partition function of the adsorbed chain. The value $c(n, m)$ is the number of configurations of polymer molecules which have $n + 1$ monomers in all (the first is fixed at the adsorbing

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** Corresponding author: Wen-qin Lu (陆文琴), E-mail: wenqinlu@yahoo.com

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surface) and m monomers (excluding the first monomer) contacting to the surface. The value μ_d is the growth constant of SAW on d -dimensional lattice, for example, $\mu_2 = 2.638$ for two-dimensional square lattice^[17] and $\mu_3 = 4.684$ for three-dimensional simple cubic lattice^[18].

Eisenriegler, Kremer, and Binder (EKB)^[1] obtained the asymptotic scaling laws for the energy at the CAP, and far away from the CAP. The mean energy $\langle E \rangle$, which is in proportional to the mean number of surface contacts $\langle m \rangle$ via $\langle E \rangle = -\langle m \rangle \varepsilon$, obeys

$$\lim_{n \rightarrow \infty} \langle E \rangle \sim \begin{cases} n^0 & \text{for } \varepsilon \ll \varepsilon_c \\ n^\phi & \text{for } \varepsilon = \varepsilon_c \\ n & \text{for } \varepsilon \gg \varepsilon_c \end{cases} \quad (2)$$

Therefore, CAP ε_c and crossover exponent ϕ can be determined by checking the power-law behavior between $\langle E \rangle$ and n .

The CAP can also be defined from the free energy difference between an adsorbed chain and a free chain in dilute solutions. There are many works^[7, 8, 19] which studied the total number of configuration, c_n , of free self-avoiding walks without surface. The number c_n obeys the scaling, $c_n \sim \mu_d^n n^{\gamma-1}$ here γ is a dimension-dependent constant. The free energy difference $\Delta F_n(\varepsilon) = F_n(\varepsilon) - \ln c_n/n$ is dependent on ε , and the CAP can be got by

$$\lim_{n \rightarrow \infty} \Delta F_n(\varepsilon) \begin{cases} = 0 & \varepsilon \leq \varepsilon_c \\ > 0 & \varepsilon > \varepsilon_c \end{cases} \quad (3)$$

for $n \rightarrow \infty$. Hence the critical absorption point can be understood as the condition where the limiting free energy of a tethered chain is equal to that of a free chain^[14, 20].

Based on the theoretical expressions (2) and (3), the values of ε_c and the crossover exponent ϕ were estimated by many studies^[3-5, 11-15]. However, different results were estimated by different methods. For example, Meirovitch and Livne^[3] obtained $\varepsilon_c = 0.291 \pm 0.001$ and $\phi = 0.530 \pm 0.007$, Rensburg and Rechnitzer^[12] estimated $\varepsilon_c = 0.288 \pm 0.020$ and $\phi = 0.5005 \pm 0.0036$, Gong and Wang^[14] estimated ε_c around 0.276 and ϕ around 0.5, and Luo^[15] got $\varepsilon_c = 0.291 \pm 0.002$ and $\phi = 0.54 \pm 0.01$ by finite-size scaling approach. Recently Descas *et al.*^[13] pointed out that a slight change in the estimation of ε_c would lead to a large deviation of ϕ .

In this paper, the number of the configurations, $c(n, m)$, of the tethered chain was counted by exactly enumerating all configurations for chain length up to 23. A function for the relation of $c(n, m)$ on n and m is derived and which is expected to be valid for long chains. Then we obtained a scaling law of the average contacting number $\langle m \rangle$, which is in good agreement with EKB. The critical point $\varepsilon_c = 0.276$ and the crossover exponent $\phi = 0.5$ was derived from the scaling. At last, we calculated the free energy difference $\Delta F_n(\varepsilon)$ and obtained ε_c which was about 0.272 by extrapolating the point at which $\Delta F_n(\varepsilon) = 0$ for short chains to that for infinite long chain. The value of ε_c was in good agreement with the result $\varepsilon_c = 0.274 \pm 0.005$ in an earlier study for longer chains with Monte Carlo method^[20].

NUMBER OF CONFIGURATIONS

In our model, a polymer molecule of length n comprises $n + 1$ self-avoiding identical monomers and each monomer occupies one lattice site in the simple cubic lattice. There is an infinitely large flat surface at $z = 0$. The surface is impenetrable for the polymer so that polymer monomers are restricted to stay in the upper half space $z \geq 0$. The first monomer of the polymer chain is fixed at site (0, 0, 0). Any monomer that is located on the surface is named as surface contact and assigned a polymer-surface interaction $-\varepsilon$.

We enumerated all configurations of single tethered chains up to chain length $n = 23$. The number of the configurations $c(n, m)$, with m surface contacts for chain length n , were recorded. Many questions could be answered if $c(n, m)$ could be determined. Unfortunately, the number of configurations increases with n nearly in

n^5 on the cubic lattice. So $c(n, m)$ s are really too large to be completely computed for longer chains. For the simple cubic lattice, Hammersley^[2] exactly enumerated $c(n, m)$ s up to $n = 14$ and Mishra^[10] up to $n = 20$. In this work we enumerated $c(n, m)$ up to chain length $n = 23$.

The dependence of $c(n, m)$ on m is plotted in Fig. 1 for chain lengths $n = 10, 15, 20$, and 23 . We find that $c(n, m)$ decreases with m except at $m = n - 1$. The value $c(n, 0)$ is the largest. The spatial configuration for $m = n$, i.e., all monomers are on the adsorbing surface, is the same as chains on a two-dimensional square lattice. We find $c(n, n)$ is much smaller than $c(n, 0)$. The value $c(n, n - 1)$ is always the smallest one and deviates obviously from the tendency of $c(n, m)$ s. In fact, we find $c(n, n - 1) = c(n - 1, n - 1)$. The reason is that, in the simple cubic lattice with surface at $z = 0$, the spatial configuration of a chain n having $n - 1$ surface contacts must have the last monomer grown in z direction from a 2D spatial configuration of chain $n - 1$. Since $c(n - 1, n - 1)$ is smaller than $c(n, n)$, so we have $c(n, n - 1) < c(n, n)$.

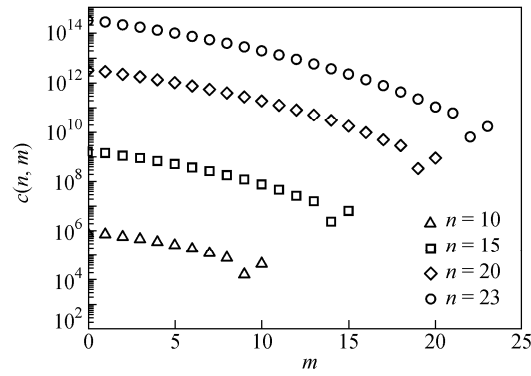


Fig. 1 Semi-logarithmic plot of the number of configurations $c(n, m)$ versus the number of surface contacts m

Figure 2 shows the dependence of $c(n, m)/c(n, 0)$ on m for different chain lengths. These curves do not locate on the same curve, indicating that the ratio $c(n, m)/c(n, 0)$ is not a simple function of m . It also depends on chain length n . We then try to figure out the function of $c(n, m)/c(n, 0)$ on n and m . We find a best candidate for the solution. When we replace horizontal variable as $x = (-0.276 + 1/n)(m + m^2/n - \ln(m + 1))$, we find that all data except the data at $m = n - 1$ collapse at the same line. The results are presented in Fig. 3. The solid line is the function $y = e^x$. In the next section, we will show that 0.276 here is just the value of CAP ε_c .

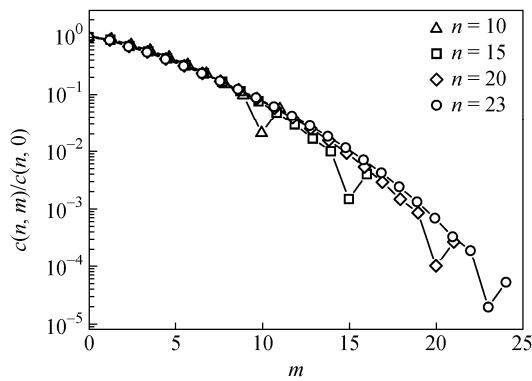


Fig. 2 Semi-logarithmic plot of $c(n, m)/c(n, 0)$ versus m for chain lengths $n = 10, 15, 20$ and 23

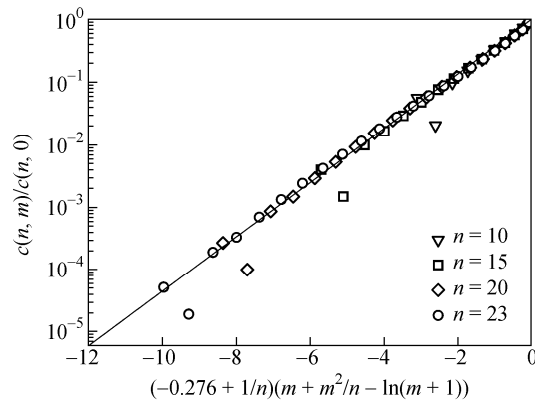


Fig. 3 Semi-logarithmic plot of $c(n, m)/c(n, 0)$ versus $x = (-0.276 + 1/n)(m + m^2/n - \ln(m + 1))$ for different chain length

From Fig. 3, we estimate that the dependence of $c(n, m)$ on n and m is

$$c(n, m) = c(n, 0) e^{(-0.276 + \frac{1}{n})(m + \frac{m^2}{n} - \ln(m+1))} \quad (4)$$

for all m except $m = n - 1$. The fitting is very good so that we expect it will hold for even longer chains. Therefore, we study the limit of average number of surface contacts by using Eq. (4) in the next section.

ENERGY OF THE TETHERED CHAIN

When m monomers of a polymer chain visit the surface at $z = 0$, the interactive energy between the chain and the surface is $E = -m\varepsilon$. We can get the average energy of chain by calculating statistical average of m , i.e. $\langle E \rangle = -\langle m \rangle \varepsilon$. From Eq. (4), we get the mean contacting number $\langle m \rangle$

$$\langle m \rangle = Z^{-1} \sum_{m=0}^n m e^{(-0.276 + \frac{1}{n})(m + \frac{m^2}{n} - \ln(m+1))} e^{m\varepsilon} \quad (5)$$

with Z is the partition function of chain. The partition function is

$$Z = \sum_{m=0}^n c(n, 0) e^{(-0.276 + \frac{1}{n})(m + \frac{m^2}{n} - \ln(m+1))} e^{m\varepsilon} \quad (6)$$

By using mathematical analysis method (see Appendix A, B and C), we get the limiting behavior of the average number of contacts $\langle m \rangle$,

$$\lim_{n \rightarrow \infty} \langle m \rangle \sim \begin{cases} n^0 & \text{for } \varepsilon \ll 0.276 \\ \sqrt{n} & \text{for } \varepsilon = 0.276 \\ n & \text{for } \varepsilon \gg 0.276 \end{cases} \quad (7)$$

This leads to the estimate of the critical point, $\varepsilon_c = 0.276$, which is in good agreement with Gong and Wang^[14], and the crossover exponent, $\phi = 0.5$, which is in good agreement with Rensburg *et al.*^[12] and Metzger *et al.*^[5].

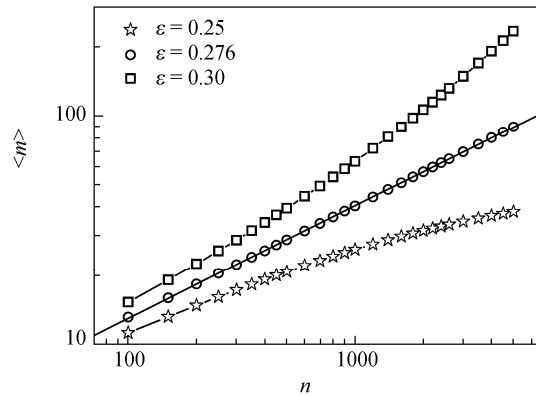


Fig. 4 lg-lg plot of average contacts $\langle m \rangle$ versus chain length n for large n from 100 to 1000 at different interactions $\varepsilon = 0.25, 0.276$ and 0.30 . The solid line at $\varepsilon = 0.276$ is the best linear fit.

Apart from using mathematical analysis methods, we also calculate the value of $\langle m \rangle$ directly from Eq. (5) for long chains. The results are plotted in Fig. 4. Two different behaviors are clearly seen: a concave upwards curve at large $\varepsilon = 0.3$ and a convex downwards curve at small $\varepsilon = 0.25$. The curve is straight at $\varepsilon = 0.276$ which

is defined as the critical point in many works^[3, 4, 15, 16]. At the critical point, the contact number has the power law $\langle m \rangle \sim n^\phi$. We find $\phi = 0.49$ from the slope of the lg-lg curve at $\varepsilon = 0.276$. The value $\phi = 0.49$ is in good agreement with 0.5 in Eq. (7). It is also consistent with several previous results^[12, 20, 21]. Figure 4 and Eq. (7) indicate that the relation Eq. (4) is very good in describing the configurational relationship for a tethered chain. We expect $\langle m \rangle$ can be measured in experiments and thus the results will be examined experimentally.

FREE ENERGY OF THE TETHERED CHAIN

The CAP also can be determined from the free energy difference between an adsorbed chain and a free chain. We have calculated the partition function $Z_n(\varepsilon) = \sum_{m=0}^n c(n, m)e^{m\varepsilon}$ for adsorbed polymer chains from exact enumeration of $c(n, m)$. The free energy per monomer of an adsorbed polymer chain, $F_n(\varepsilon) = \frac{1}{n} \ln Z_n(\varepsilon)$, is dependent on the interaction strength ε . The free energy difference between an adsorbed chain and a free chain, $\Delta F_n(\varepsilon)$, is plotted in Fig. 5. The interaction at which $\Delta F_n(\varepsilon) = 0$ is defined as the critical point $\varepsilon_c(n)$ for finite chain length^[20]. We notice that $\varepsilon_c(n)$ increases with n . The $\varepsilon_c(n)$ is expected to depend on n in a scaling law^[19] as $\varepsilon_c(n) = \varepsilon_c(\infty) - \alpha n^{-0.5}$, and $\varepsilon_c(\infty)$ is the CAP at infinite chain length limit. The inset of Fig. 5 shows the linear fitting of $\varepsilon_c(n)$ versus $n^{-0.5}$ for n from 13 up to 23, which yields $\varepsilon_c(\infty) = 0.272$. The value 0.272 is close to 0.274 ± 0.005 determined from energy difference^[20], where free energy was calculated by Monte Carlo method for chain length up to $n = 200$.

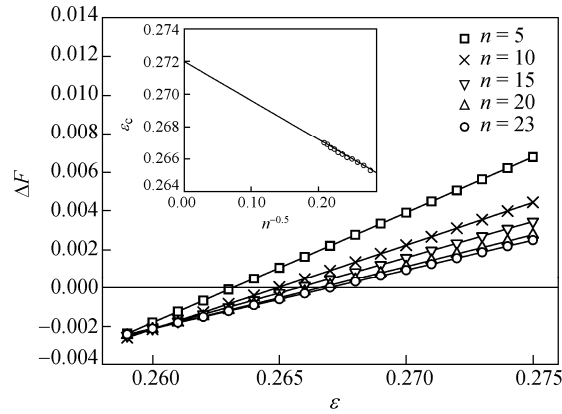


Fig. 5 Plot of ΔF versus ε for SAW chains $n = 5, 10, 15, 20$ and 23

The inset presents $\varepsilon_c(n)$ versus $n^{-0.5}$ where $\varepsilon_c(n)$ is extracted from $\Delta F_n(\varepsilon) = 0$ for n from 13 up to 23.

CONCLUSIONS

In this paper, we enumerate exactly all configurations of free and tethered SAW chains up to length $n = 23$ on the simple cubic lattice. We record the number of the configurations $c(n, m)$ with m surface contacts. We obtain a function describing the relation of $c(n, m)$ on m and n . The mean surface contacts $\langle m \rangle$ of a tethered chain on adsorbing surface are calculated from the function. The scaling between $\langle m \rangle$ and n at different ε is in good agreement with EKB. We get the critical adsorption point $\varepsilon_c = 0.276$ and the crossover exponent $\phi = 0.5$. We have also studied the free energy difference $\Delta F_n(\varepsilon)$ between a tethered chain and a free chain. The critical point $\varepsilon_c(n)$ is determined from $\Delta F_n(\varepsilon) = 0$, and $\varepsilon_c(n)$ is expected to depend on n as $\varepsilon_c(n) = \varepsilon_c(\infty) - \alpha n^{-0.5}$. Then we get $\varepsilon_c \cong 0.272$ for infinite chains. Our results of ε_c and ϕ are consistent with those of earlier studies.

APPENDIX

A. LEMMA 1

Lemma 1. If $\langle m \rangle = \frac{\sum_{m=0}^n m e^{(-a+\frac{1}{n})(m+\frac{m^2}{n}-\ln(m+1))}}{\sum_{m=0}^n e^{(-a+\frac{1}{n})(m+\frac{m^2}{n}-\ln(m+1))}}$, where a is a positive constant, then

$$\lim_{n \rightarrow \infty} \langle m \rangle \sim \begin{cases} n^0 & \text{for } x \ll a \\ \sqrt{n} & \text{for } x = a \\ n & \text{for } x \gg a \end{cases} \quad (\text{A1})$$

Proof. From Lemma 2 (see Appendix B), we get

$$\lim_{n \rightarrow \infty} \langle m \rangle = A \lim_{n \rightarrow \infty} \frac{\sum_{m=1}^n m^{1+a} e^{m(x-a-\frac{m}{n}a)}}{\sum_{m=1}^n m^a e^{m(x-a-\frac{m}{n}a)}}$$

Step 1. We proof Eq. (A1) for $x \ll a$.

$$A \lim_{n \rightarrow \infty} \frac{\sum_{m=1}^n m^{1+a} e^{m(x-a-\frac{a}{n})}}{\sum_{m=1}^n m^a e^{m(x-2a)}} > \lim_{n \rightarrow \infty} \langle m \rangle > A \lim_{n \rightarrow \infty} \frac{\sum_{m=1}^n m^{1+a} e^{m(x-2a)}}{\sum_{m=1}^n m^a e^{m(x-a-\frac{a}{n})}}$$

When $x < a$, we get $x - 2a < 0$. Therefore,

$$\lim_{m \rightarrow \infty} m^{3+a} e^{m(x-2a)} = \lim_{m \rightarrow \infty} \frac{m^{3+a}}{e^{m(2a-x)}} = 0$$

$$\lim_{m \rightarrow \infty} m^{1+a} e^{m(x-2a)} = 0 \left(\frac{1}{m^2} \right)$$

So $\lim_{n \rightarrow \infty} \sum_{m=1}^n m^{1+a} e^{m(x-2a)}$ is finite. By the same way, we can get, $\lim_{n \rightarrow \infty} \sum_{m=1}^n m^{1+a} e^{m(x-a-\frac{a}{n})}$, $\lim_{n \rightarrow \infty} \sum_{m=1}^n m^a e^{m(x-2a)}$ and

$\lim_{n \rightarrow \infty} \sum_{m=1}^n m^a e^{m(x-a-\frac{a}{n})}$ are finite. Therefore, we obtain

$$\lim_{n \rightarrow \infty} \langle m \rangle \sim n^0 \quad \text{for } x \ll a$$

Step 2. We proof Eq. (A1) for $x = a$.

When $x = a$, we get

$$\lim_{n \rightarrow \infty} \langle m \rangle = A \lim_{n \rightarrow \infty} \frac{\sum_{m=1}^n m^{1+a} e^{-a\frac{m^2}{n}}}{\sum_{m=1}^n m^a e^{-a\frac{m^2}{n}}} \approx A \frac{\int_0^\infty m^{1+a} e^{-a\frac{m^2}{n}} dm}{\int_0^\infty m^a e^{-a\frac{m^2}{n}} dm} = A \sqrt{\frac{n}{a}} \frac{\Gamma(\frac{a}{2}+1)}{\Gamma(\frac{a}{2}+\frac{1}{2})}$$

where $\Gamma(\frac{a}{2}+1)$ and $\Gamma(\frac{a}{2}+\frac{1}{2})$ are Γ -Functions. So when $x = a$, we get

$$\lim_{n \rightarrow \infty} \langle m \rangle \sim \sqrt{n} \quad \text{for } x = a$$

Step 3. We proof Eq. (A1) for $x \gg a$.

$$\sup(\lim_{n \rightarrow \infty} \langle m \rangle) = \lim_{n \rightarrow \infty} A \frac{\sum_{m=1}^n n m^a e^{m(x-a-\frac{m}{n}a)}}{\sum_{m=1}^n m^a e^{m(x-a-\frac{m}{n}a)}} = An \quad (A2)$$

Since $x \gg a$, we get $x - a - \frac{m}{n}a > 0$. From Lemma 3 (see Appendix C), we know that $\lim_{n \rightarrow \infty} \langle m \rangle$ increase with $(x - a - ma/n)$. The minimum value of $x - a - ma/n$ in expression of $\lim_{n \rightarrow \infty} \langle m \rangle$ is $x - 2a$, we obtain

$$\lim_{n \rightarrow \infty} \langle m \rangle > A \lim_{n \rightarrow \infty} \frac{\sum_{m=1}^n m^{1+a} e^{m(x-2a)}}{\sum_{m=1}^n m^a e^{m(x-2a)}} > A \lim_{n \rightarrow \infty} \frac{n^{1+a} e^{n(x-2a)}}{n^a \sum_{m=1}^n e^{m(x-2a)}} = An$$

So we obtain

$$\inf(\lim_{n \rightarrow \infty} \langle m \rangle) = An \quad (A3)$$

From equations (A2) and (A3), we get

$$\lim_{n \rightarrow \infty} \langle m \rangle \sim n \quad \text{for } x \gg a$$

B. LEMMA 2

$$\text{Lemma 2} \quad \lim_{n \rightarrow \infty} \frac{\sum_{m=0}^n m e^{(-a+\frac{1}{n})(m+\frac{m^2}{n}-\ln(m+1))} e^{mx}}{\sum_{m=0}^n e^{(-a+\frac{1}{n})(m+\frac{m^2}{n}-\ln(m+1))} e^{mx}} = A \lim_{n \rightarrow \infty} \frac{\sum_{m=1}^n m^{1+a} e^{m(x-a-\frac{m}{n}a)}}{\sum_{m=1}^n m e^{m(x-a-\frac{m}{n}a)}}$$

where A is a number between $(\frac{1}{2^{a+1}e^2}, 2^a e^2)$, a is a positive constant.

Proof. The maximum value of $\frac{m}{n} + \frac{m^2}{n^2} - \frac{1}{n} \ln(m+1)$ with m between $[0, n]$ is $2 - \frac{1}{n} \ln(n+1)$ as $m = n$ and the minimum value of that is 0 as $m = 0$. If we take the maximum value of the numerator and the minimum value of the denominator, we get

$$\lim_{n \rightarrow \infty} \frac{\sum_{m=0}^n m e^{(-a+\frac{1}{n})(m+\frac{m^2}{n}-\ln(m+1))} e^{mx}}{\sum_{m=0}^n e^{(-a+\frac{1}{n})(m+\frac{m^2}{n}-\ln(m+1))} e^{mx}} < e^2 \lim_{n \rightarrow \infty} \frac{\sum_{m=0}^n m e^{-a(m+\frac{m^2}{n}-\ln(m+1))} e^{mx}}{\sum_{m=0}^n e^{-a(m+\frac{m^2}{n}-\ln(m+1))} e^{mx}} < 2^a e^2 \lim_{n \rightarrow \infty} \frac{\sum_{m=1}^n m e^{-a(m+\frac{m^2}{n}-\ln m)} e^{mx}}{\sum_{m=1}^n e^{-a(m+\frac{m^2}{n}-\ln m)} e^{mx}}$$

Therefore,

$$\sup(\lim_{n \rightarrow \infty} \frac{\sum_{m=0}^n m e^{(-a+\frac{1}{n})(m+\frac{m^2}{n}-\ln(m+1))} e^{mx}}{\sum_{m=0}^n e^{(-a+\frac{1}{n})(m+\frac{m^2}{n}-\ln(m+1))} e^{mx}}) = 2^a e^2 \lim_{n \rightarrow \infty} \frac{\sum_{m=1}^n m^{1+a} e^{-a(m+\frac{m^2}{n})} e^{mx}}{\sum_{m=1}^n m^a e^{-a(m+\frac{m^2}{n})} e^{mx}}$$

If we take the minimum value of the numerator and the maximum value of the denominator, we get

$$\lim_{n \rightarrow \infty} \frac{\sum_{m=0}^n m e^{(-a+\frac{1}{n})(m+\frac{m^2}{n}-\ln(m+1))} e^{mx}}{\sum_{m=0}^n e^{(-a+\frac{1}{n})(m+\frac{m^2}{n}-\ln(m+1))} e^{mx}} > \frac{1}{2^{a+1} e^2} \lim_{n \rightarrow \infty} \frac{\sum_{m=1}^n m e^{-a(m+\frac{m^2}{n}-\ln m)} e^{mx}}{\sum_{m=1}^n e^{-a(m+\frac{m^2}{n}-\ln m)} e^{mx}}$$

Therefore,

$$\inf \left(\lim_{n \rightarrow \infty} \frac{\sum_{m=0}^n m e^{(-a+\frac{1}{n})(m+\frac{m^2}{n}-\ln(m+1))} e^{mx}}{\sum_{m=0}^n e^{(-a+\frac{1}{n})(m+\frac{m^2}{n}-\ln(m+1))} e^{mx}} \right) = \frac{1}{2^{a+1} e^2} \lim_{n \rightarrow \infty} \frac{\sum_{m=1}^n m^{1+a} e^{-a(m+\frac{m^2}{n})} e^{mx}}{\sum_{m=1}^n m^a e^{-a(m+\frac{m^2}{n})} e^{mx}}$$

C. LEMMA 3

Lemma 3. $f(x) = \frac{\sum_{m=1}^n m^{1+a} e^{mx}}{\sum_{m=1}^n m^a e^{mx}}$ increases with x increasing for $x > 0$.

Proof. $f'(x) = \frac{\sum_{m=1}^n m^{2+a} e^{mx}}{\sum_{m=1}^n m^a e^{mx}} - \sum_{m=1}^n m^{1+a} e^{mx} \frac{\sum_{m=1}^n m^{1+a} e^{mx}}{(\sum_{m=1}^n m^a e^{mx})^2}$

(1) For $n = 1$, $f_{n=1}'(x) = 0$

(2) For $n = 2$, $f_{n=2}'(x) = \frac{2^a e^{3x}}{(e^x + 2^a e^{2x})^2} > 0$

(3) For $n = k$, we assume $f_{n=k}'(x) = \frac{\sum_{m=1}^k m^{2+a} e^{mx}}{\sum_{m=1}^k m^a e^{mx}} - \frac{(\sum_{m=1}^k m^{1+a} e^{mx})^2}{(\sum_{m=1}^k m^a e^{mx})^2} > 0$

We write it as $f_{n=k}'(x) = \frac{b_2}{b_0} - \frac{b_1^2}{b_0^2} = \frac{b_2 b_0 - b_1^2}{b_0^2} > 0$

Where $b_1 = \sum_{m=1}^k m^{1+a} e^{mx}$,

$b_0 = \sum_{m=1}^k m^a e^{mx}$,

$b_2 = \sum_{m=1}^k m^{2+a} e^{mx} = e^x + \sum_{m=2}^k m m^{1+a} e^{mx} > e^x + 2 \sum_{m=2}^k m^{1+a} e^{mx} = 2b_1 - e^x$

We get

$$f_{n=k+1}'(x) = \frac{b_2 + (k+2)e^{(k+2)x}}{b_0 + (k+1)e^{(k+1)x}} - \frac{(b_1 + (k+1)e^{(k+1)x})^2}{(b_0 + (k+1)e^{(k+1)x})^2} > 0$$

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