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Model of inverse "dry" micelles with coexisting spherical, globular and cylindrical aggregates

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Corresponding Author:	Alexander K Shchekin, Dr.Sc., Ph.D. St Petersburg University St Petersburg, RUSSIAN FEDERATION
First Author:	Yuri A. Eroshkin, M.Sc.
Order of Authors:	Yuri A. Eroshkin, M.Sc.
	Loran Ts Adzhemyan, D.Sc.
	Alexander K Shchekin, Dr.Sc., Ph.D.
Abstract:	A new statistical thermodynamic model of inverse nonionic aggregates of surfactant molecules in nonpolar solvents is considered. This model admits the fluctuation coexistence of inverse spherical, globular, and spherocylindrical aggregates without activation barriers between them. The model is based on the assumption of a uniform bulk density of the number of molecular groups inside the core of an aggregate that can continuously transform into a sphere, a globule, and a spherocylinder. In this model, for any aggregation numbers, the work of aggregation depends not only on the aggregation numbers and the concentration of surfactant monomers, but also on two independent geometric parameters characterizing, at the same aggregation numbers, the deviation from the spherical form of the aggregate towards globular and spherocylindrical forms. Even in the range of small aggregation numbers, this fact leads to a significant difference between the equilibrium distribution function of aggregates, which depends on the aggregation number and two form parameters, and the one-dimensional distribution function in terms of aggregation numbers. It is shown that the optimal values of the form parameters, which minimize the work of aggregation, are in good agreement for spherocylindrical aggregates with the predictions of a purely geometric model of such aggregates under the additional assumption of a uniform surface density of molecular groups at the micelle core. The predictions of a new molecular thermodynamic model for the degrees of surfactant micellization in inverse aggregates of various forms at different surfactant concentrations are considered.
Suggested Reviewers:	Kenichiro Koga, Ph.D. Professor, Okayama University koga@cc.okayama-u.ac.jp He is a well-known specialist in thermodynamics and kinetics of hydrophobic effect, aggregation in solutions, in particular, micellar solutions.
	Gennady Gor, Ph.D. Associate Professor, New Jersey Institute of Technology, USA gor@njit.edu He is a known specialist in kinetics of nucleation, dispersed systems, solutions, statistical mechanics
	Elena N Brodskaya, D.Sc. St Petersburg University elena_brodskaya@mail.ru She is a recognized specialist in modeling of micellar solutions
	James T Kindt, Ph.D. Professor, Emory University

	jkindt@emory.edu He is a well-known specialist in thermodynamics and kinetics of aggregation in solutions, in particular, micellar solutions.
	Tamara G Movchan, Ph.D. Senior Research Fellow, Frumkin Institute of Physical Chemistry and Electrochemistry RAS movchan_tamara@mail.ru She is a known specialist in the experiment on direct and inverse micelles

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Dear Editor,

We would like to submit our paper “Model of inverse "dry" micelles with coexisting spherical, globular and cylindrical aggregates” by Yury Eroshkin, Loran Adzhemyan, and Alexander Shchekin for publication in Physica A: Statistical Mechanics and its Applications as a research article.

In this manuscript, a new statistical thermodynamic model of inverse non-ionic aggregates of surfactant molecules in non-polar solvents is described. The model allows fluctuation coexistence of spherical, globular, and spherocylindrical aggregates without activation barriers between them. It is shown that for any aggregation numbers in this model, the work of aggregation depends not only on the aggregation numbers and the concentration of surfactant monomers, but also on the parameters characterizing the deviation from the spherical form of the aggregate towards globular and spherocylindrical aggregates. A method for estimating the normalization factor for the distribution of aggregates by aggregation numbers and form parameters is proposed, which makes it possible to find the degree of micellization of a surfactant solution in the presence of micelles of different forms. It is shown that the optimal values of the form parameters, which minimize the work of aggregation, are in good agreement for spherocylindrical aggregates with the predictions of a purely geometric model of such aggregates under the additional assumption of a uniform surface density of molecular groups on the micelle core.

We hope that the results presented in the manuscript will be of interest for the audience of Physica A: Statistical Mechanics and its Applications.

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On behalf of all contributors,

Alexander K. Shchekin

HIGHLIGHTS

- A new statistical thermodynamic model of inverse nonionic micelles is proposed.
- Model admits the fluctuational coexistence of inverse spherical, globular, and spherocylindrical micelles.
- Predictions for the degrees of micellization in inverse aggregates of various forms are given.

CORRESPONDING AUTHOR Prof. Alexander Shchekin
AUTHOR'S PHONE NUMBER +7 911 9495666

AUTHOR'S FAX NUMBER +7 812 4287240
AUTHOR'S EMAIL akshch@list.ru
AUTHOR'S POSTAL ADDRESS: Statistical Physics Department, Faculty of Physics, St Petersburg State University, Ulyanovskaya 1, Stary Peterhof, St Petersburg, 198504 Russia

Model of inverse "dry" micelles with coexisting spherical, globular and cylindrical aggregates

Yu.A. Eroshkin[1], L.Ts. Adzhemyan[1,2], A.K. Shchekin[1]*

[1]*Department of Physics, St. Petersburg State University, 7/9 Universitetskaya nab., St. Petersburg, 199034, Russia*
[2]*Bogoliubov Laboratory of Theoretical Physics, Joint Institute for Nuclear Research,6 Joliot-Curie, Dubna, Moscow Region, 141980, Russia*
**E-mail: akshch@list.ru*

A new statistical thermodynamic model of inverse nonionic aggregates of surfactant molecules in nonpolar solvents is considered. This model admits the fluctuation coexistence of inverse spherical, globular, and spherocylindrical aggregates without activation barriers between them. The model is based on the assumption of a uniform bulk density of the number of molecular groups inside the core of an aggregate that can continuously transform into a sphere, a globule, and a spherocylinder. In this model, for any aggregation numbers, the work of aggregation depends not only on the aggregation numbers and the concentration of surfactant monomers, but also on two independent geometric parameters characterizing, at the same aggregation numbers, the deviation from the spherical form of the aggregate towards globular and spherocylindrical forms. Even in the range of small aggregation numbers, this fact leads to a significant difference between the equilibrium distribution function of aggregates, which depends on the aggregation number and two form parameters, and the one-dimensional distribution function in terms of aggregation numbers. It is shown that the optimal values of the form parameters, which minimize the work of aggregation, are in good agreement for spherocylindrical aggregates with the predictions of a purely geometric model of such aggregates under the additional assumption of a uniform surface density of molecular groups at the micelle core. The predictions of a new molecular thermodynamic model for the degrees of surfactant micellization in inverse aggregates of various forms at different surfactant concentrations are considered.

INTRODUCTION

The creation of a molecular thermodynamic model capable of explaining the mechanism of surfactant aggregation in a nonpolar solvent in the absence of water, predicting the critical micelle concentration (CMC), forms and characteristic numbers of aggregation of “dry” (i.e., without water molecules in the micelle core) inverse micelles is an actual task. Experimental works [1–3] and molecular dynamics and thermodynamic modeling of inverse micelles [4–6] show that CMC and dry inverse nonionic and ionic micelles actually exist in nonpolar solutions, and their

form may differ from a spherical one. Recently we have derived [7], based on the extended droplet model of micelles, an analytical expression for the minimal work of aggregation of inverse spherical micelles. This expression was constructed taking into account the contributions due to electrostatic interactions of the surfactant polar heads in the inverse micelle core, the effects of the conformation of hydrocarbon tails in the micellar crown and polar heads in the micellar core, the effects of the excluded area on the surface of the micelle core described by two-dimensional equation of the theory of scaled particles [8]. In general terms, the constructed expression for the work of aggregation did not depend on the form of the aggregates, and in the case of spherical inverse micelles it predicted the existence of CMC and made it possible to find the equilibrium distribution of micelles over the aggregation numbers.

It is usually accepted that various forms of micelles, among which spherical, globular, and spherocylindrical micelles are distinguished, arise sequentially with an increase in the total surfactant concentration in a solution. In such a case, the first CMC is associated with spherical micelles, the second CMC is associated with the accumulation of a significant proportion of surfactants in spherocylindrical micelles. The first thermodynamic models for spherical, globular, and spherocylindrical micelles were proposed in [9–11] and later expanded in [12–17]. Based on these models, the micelle formation kinetics was considered taking into account transitions between different forms of micelles [18–33]. There were studied situations when several potential humps separated by potential minima appear in the aggregation work as a function of the aggregation number with increasing total surfactant concentration, as well as situations where the aggregation work has several separate branches corresponding to micelles of different forms.

In this paper, we consider a new statistical thermodynamic model of non-ionic inverse aggregates of surfactant molecules in non-polar solvents, which allows for the fluctuation coexistence of spherical, globular, and spherocylindrical aggregates without activation barriers between them. According to this model, the minimal work of aggregation for any aggregation numbers will depend not only on the aggregation numbers and concentration of surfactant monomers, but also on two geometric parameters that characterize the deviation from the spherical form of the aggregate towards globular and spherocylindrical aggregates. Thus, it is assumed that for the same aggregation numbers, globular and spherocylindrical inverse aggregates can exist together with spherical inverse aggregates. Below we will see that even in the range of small aggregation numbers, this assumption leads to a significant difference between the equilibrium distribution function of aggregates, which now depends on three internal variables, and the one-dimensional distribution function in aggregation numbers only. Our task will be to investigate the optimal values of the form parameters for globular and spherocylindrical aggregates and construct the corresponding optimal one-dimensional aggregation work of inverse dry micelles, to consider

the integral one-dimensional aggregation work of micelles, which would determine the concentration of surfactant aggregates of any form with the given aggregation number, to find the first and second CMC within the framework of the proposed model and to calculate the relative fractions of short and long micelles depending on the concentration of surfactant monomers.

1. FORMS OF MOLECULAR AGGREGATES AND INITIAL ASSUMPTIONS

Let us consider an aggregate of surfactant molecules, which, at various values of the form parameters, continuously transforms into a sphere, a globule, and a spherical cylinder. The shape of core of such an aggregate is shown in Fig.1. Here, the form parameter λ expressed in units of the radius r of the spherical part of the aggregate shows the length of the cylindrical part of the micelle. The parameter λ changes in the interval $[0;\infty)$, it is zero for spheres and globules and strictly greater than zero for cylinders.

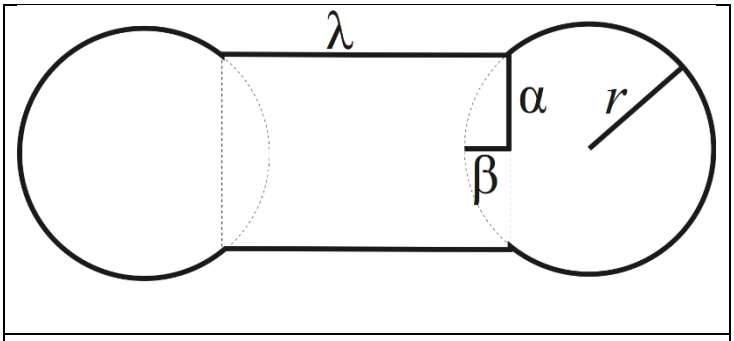

Fig.1. Shape of the inverse micellar core.

Also expressed in units of radius r, the form parameter β shows the depth of entry of the spheres into the cylindrical part of the aggregate. The parameter β varies in the interval $(0,1]$, $\beta=1$ for spheres and β is strictly less than 1 for globules. Parameters β and λ will be important additional independent variables in the model what follows.

Figure 1 also shows the additional parameter α (also expressed in units of radius r), which is equal to the radius of the excluded spherical segment, and which coincides with the cylinder radius in the presence of a cylindrical part of the aggregate. The parameter α changes in the interval $(0,1]$ and is equal to 1 for spherical aggregates, $\alpha<1$ for globules. This parameter is of interest, since it was previously discussed in the literature [14] with certain fixed estimates. Figure 1 shows that this parameter can be expressed through the parameter β as

$$\alpha=\sqrt{\beta(2-\beta)}\,. \tag{1.1}$$

With the help of parameters β and λ it is possible to express the area S and the volume V of the aggregate in the form

$$S=S_{\text{sph}}+S_{\text{cyl}},\ V=V_{\text{sph}}+V_{\text{cyl}}\,, \tag{1.2}$$

where S_{sph} and S_{cyl} are the areas of the spherical and, respectively, the cylindrical part of the aggregate, V_{sph} and V_{cyl} are the volumes of the spherical and, respectively, the cylindrical part of the aggregate. For S_{sph} and S_{cyl}, V_{sph} and V_{cyl}, we find

$$S_{\text{sph}} = 4\pi r^2 (2-\beta), \tag{1.3}$$

$$S_{\text{cyl}} = 2\pi r^2 \lambda \sqrt{\beta(2-\beta)}, \tag{1.4}$$

$$V_{\text{sph}} = \frac{2}{3}\pi r^3 (2-\beta)^2 (1+\beta), \tag{1.5}$$

$$V_{\text{cyl}} = \pi r^3 \beta(2-\beta)\lambda. \tag{1.6}$$

Let the total number of surfactant molecules in the aggregate be equal to n. Let us denote the number of surfactant molecules in the spherical part of the aggregate as n_{sph}, and that in the cylindrical part as n_{cyl}, so that $n = n_{\text{sph}} + n_{\text{cyl}}$. Let us assume that the bulk density of the number of head (polar) molecular groups inside the core of inverse micelle is uniform, i.e. the quantity

$$\frac{n_{\text{sph}}}{V_{\text{sph}}} = \frac{n_{\text{cyl}}}{V_{\text{cyl}}} = \frac{n}{V} = \frac{1}{\upsilon_{\text{p}}} \tag{1.7}$$

has a fixed value, where υ_{p} is the volume of the head group of the surfactant molecule. Then equalities (1.5) and (1.6) implies an expression for the relationship between the total aggregation number and the radius r of the spherical part of the spherocylindrical core of the aggregate for given parameters β and λ in the form:

$$r(n,\beta,\lambda) = n^{1/3} \sqrt[3]{\frac{3\upsilon_{\text{p}}/\pi}{2(2-\beta)^2(1+\beta)+3\beta(2-\beta)\lambda}}, \quad 0<\beta\le 1,\ \lambda \ge 0. \tag{1.8}$$

In particular, for spherical aggregates at $\beta = 1$ and $\lambda = 0$ we find from eq.(1.8)

$$r(n) = n^{1/3} \sqrt[3]{3\upsilon_{\text{p}}/4\pi}, \tag{1.9}$$

and for globular aggregates at $\lambda = 0$, we obtain

$$r(n,\beta) = n^{1/3} \sqrt[3]{\frac{3\upsilon_{\text{p}}/\pi}{2(2-\beta)^2(1+\beta)}}, \ 0<\beta<1. \tag{1.10}$$

We see that $r(n) > r(n,\beta) \ge r(n,\beta,\lambda)$.

2. AGGREGATION WORK AND OPTIMAL VALUES OF FORM PARAMETERS

Let us write the expression obtained in [7] for the minimal work of aggregation of inverse micelles. In thermal units $k_{\mathrm{B}}T$, k_{B} is the Boltzmann constant, T is the absolute temperature of the solution, taking into account eqs.(1.2) and (1.7) at $n >> 1$, we have

$$W = \frac{\gamma\left(S_{sph} + S_{\mathrm{cyl}}\right)}{k_{\mathrm{B}}T} - n\left(B_{\mathrm{el}} + \ln \upsilon_{\mathrm{p}} c_1\right) + \frac{\left(3 - \dfrac{2n_{\mathrm{sph}}a_0}{S_{\mathrm{sph}}}\right)\dfrac{n_{sph}^2 a_0}{S_{\mathrm{sph}}}}{\left(1 - \dfrac{n_{\mathrm{sph}}a_0}{S_{\mathrm{sph}}}\right)^2} + \frac{\left(3 - \dfrac{2n_{\mathrm{cyl}}a_0}{S_{\mathrm{cyl}}}\right)\dfrac{n_{\mathrm{cyl}}^2 a_0}{S_{\mathrm{cyl}}}}{\left(1 - \dfrac{n_{\mathrm{cyl}}a_0}{S_{\mathrm{cyl}}}\right)^2} +$$

$$+ \frac{1}{2}\left(b^2 + \frac{2}{b} - 3\right)n - n_{\mathrm{sph}} \ln\left(1 - \frac{n_{\mathrm{sph}}a_0}{S_{\mathrm{sph}}}\right) - n_{\mathrm{cyl}} \ln\left(1 - \frac{n_{\mathrm{cyl}}a_0}{S_{\mathrm{cyl}}}\right). \qquad (2.1)$$

Here, γ is the interfacial tension at the boundary between the aggregate core and the solution, B_{el} is a positive dimensionless quantity characterizing the electrostatic interactions of bound charges that make up the polar groups of surfactant molecules, c_1 is the bulk concentration of surfactant monomers in the solution, a_0 is the cross-sectional area of that part of the surfactant molecule that intersects the surface of the aggregate core, b is the extension parameter related to the effective thickness of the aggregate crown [7]. Numerical estimates for the lattice model of a "dry" inverse micelle in [34] and molecular dynamics modeling of $C_{12}E_4$ inverse micelles in heptane in [6] showed that the quantity $B_{\mathrm{el}} >> 1$, B_{el} depends on temperature and tends to become constant at $n >> 1$. Taking into account eqs.(1.3) - (1.8), expression (2.1) determines the dimensionless work W of aggregation as a function of the aggregation number n, parameters β, λ and concentration of surfactant monomers c_1. Since the work on formation of an aggregate from a single surfactant monomer is equal to zero, then the work of aggregation W must be additionally defined as $W\left(n = 1, \beta, \lambda, c_1\right) = 0$.

It is easy to check that for spherical aggregates with $\lambda = 0$ and $\beta = 1$ eq.(2.1) with the extension $W\left(n = 1, \beta, \lambda, c_1\right) = 0$ transforms into

$$W\left(n, c_1\right) = \frac{4\pi\gamma}{kT}\omega^2 n^{2/3} - \left(\ln \upsilon_{\mathrm{p}} c_1 + B_{\mathrm{el}}\right)n + \frac{\left(3 - a_0 n^{1/3}/2\pi\gamma\omega^2\right)a_0/4\pi\gamma\omega^2}{\left(1 - a_0 n^{1/3}/4\pi\gamma\omega^2\right)^2} n^{4/3} +$$

$$+ \frac{1}{2}\left(b^2 + \frac{2}{b} - 3\right)n - n\ln\left(1 - a_0 n^{1/3}/4\pi\gamma\omega^2\right), \qquad (2.2)$$

$$W\left(n = 1, c_1\right) = 0, \qquad (2.3)$$

where

$$\omega \equiv \left(3\upsilon_{\rm p}/4\pi\right)^{1/3}. \tag{2.4}$$

Let us choose the following values of the thermodynamic parameters of the problem (using the data for a solution of $C_{12}E_4$ surfactant molecules in heptane [7]):

$$T = 293\,\text{K},\ \ \gamma = 0.030\,\text{N/m},\ \upsilon_{\rm p} = 2.484\times10^{-28}\,\text{m}^3,\ \omega = 3.9\cdot10^{-10}\,\text{m},$$

$$B_{\rm el} = 20,\quad c_{10} = 1.35\times10^{22}\,\text{m}^{-3},\quad a_0 = 21\cdot10^{-20}\,\text{m}^2,\quad b = 2. \tag{2.5}$$

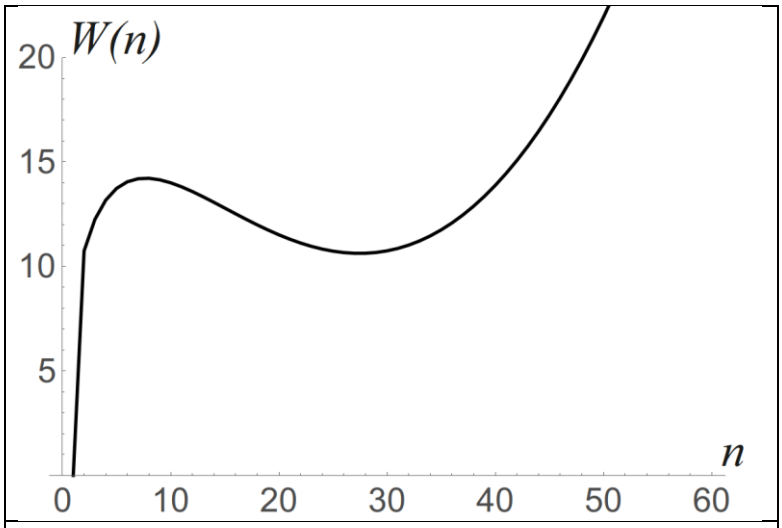

Fig.2. Work of aggregation of a spherical inverse micelle, constructed from eq.(2.2) by substitution eq.(2.5).

We took in (2.5) the value of the concentration of surfactant monomers $c_1 = c_{10}$ in such a way that, the work $W\left(n, c_1\right)$, with the values from eq.(2.5) substituted in eq.(2.2), had a pronounced maximum at $n = 8$ and a minimum at $n = 28$. The corresponding curve of the aggregation work $W\left(n, c_{10}\right)$ as a function of the aggregation number n is shown in Fig.2.

The optimal values of the form parameters λ and β at minimizing the work W of aggregation of an inverse micelle with a spherical, globular, or spherocylindrical form (corresponding to Fig. 1), given by eq.(2.1) together with eqs.(1.2)–(1.7), can be sought for each value of the aggregation number n from the conditions

$$\left.\frac{\partial W\left(n,\beta,\lambda,c_1\right)}{\partial\lambda}\right|_{\lambda=\lambda_{opt}(n),\beta=\beta_{opt}(n)} = 0, \tag{2.6a}$$

$$\left.\frac{\partial W\left(n,\beta,\lambda,c_1\right)}{\partial\beta}\right|_{\lambda=\lambda_{opt}(n),\beta=\beta_{opt}(n)} = 0. \tag{2.6b}$$

Let us consider the dependences of the optimal parameters $\beta_{\rm opt}$ and $\lambda_{\rm opt}$ on the aggregation number n, which follow from eqs. (2.6). These dependencies are shown in Figs. 3 and 4. The first vertical line in these figures at $n = 35$ marks the point at which the "optimal" micelle grows like a sphere. This is indicated by the values $\beta_{\rm opt} = 1$ and $\lambda_{\rm opt} = 0$ at $n < 35$.

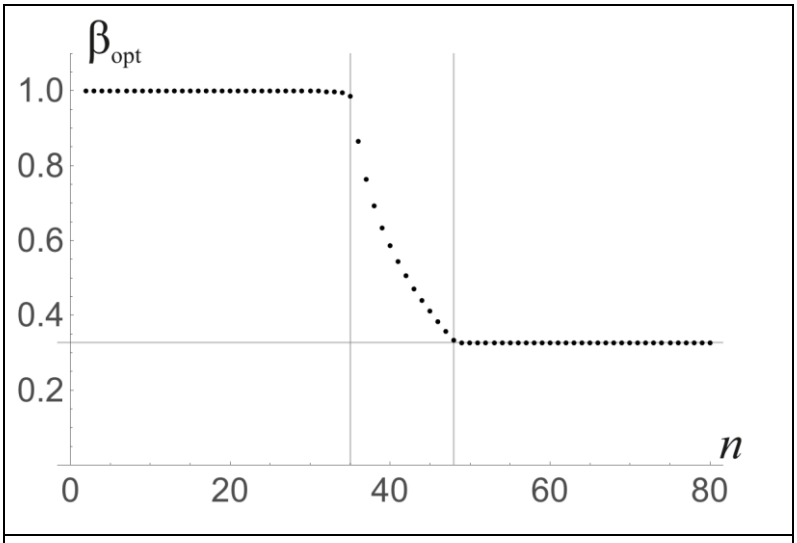

Fig.3. Dependence of β_{opt} on the aggregation number n.

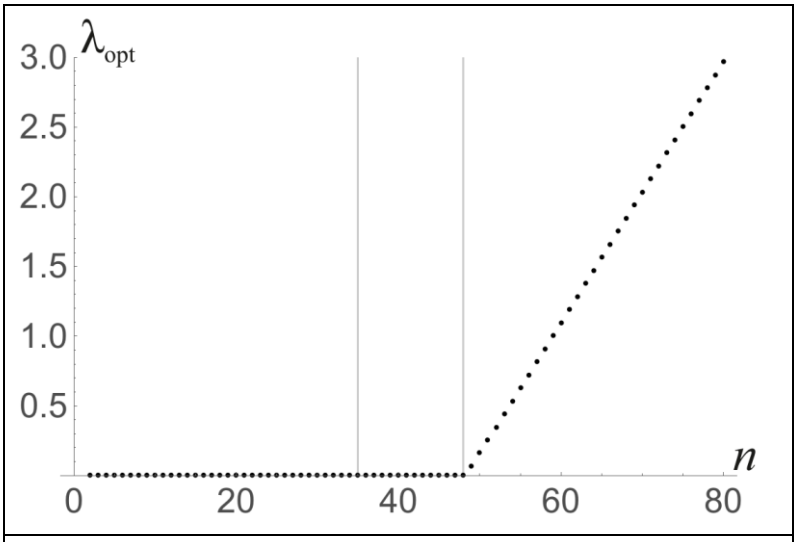

Fig.4. Dependence of λ_{opt} on the aggregation number n.

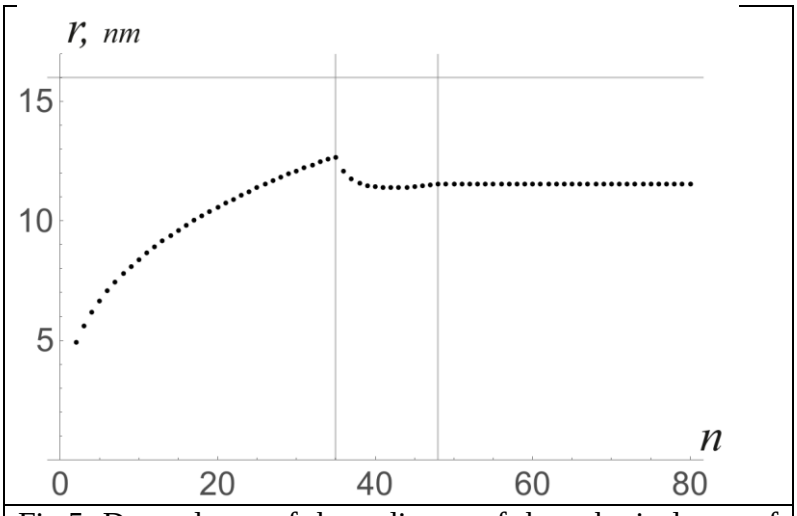

Fig.5. Dependence of the radius r of the spherical part of the aggregate core on the aggregation number n at $\beta = \beta_{opt}$ and $\lambda = \lambda_{opt}$.

As seen from Fig. 3, at the very point $n = 35$ the micelle turns into a globule, and between the first and second vertical lines in Fig. 3 there is a decrease in the parameter β_{opt} until it finally reaches a constant value, starting from the second vertical line at $n = 48$.

As follows from Fig. 4, at the point $n = 48$ marked by the second vertical line, the micelle turns into a spherocylinder (begins to increase the cylindrical part in Fig. 1) and further grows only due to elongation of cylindrical part, since β_{opt} in Fig. 3 at $n > 48$ retains its value $\beta_{opt} = 0.32748$. The above is confirmed by the dependence on n of the radius $r\left(n, \beta_{opt}, \lambda_{opt}\right)$ of the spherical parts of the aggregate core, plotted in Fig. 5 according to eq. (1.8) with the optimal dependences of the parameters β_{opt} and λ_{opt} corresponding to Figs. 3 and 4. Figure 5 shows that up to the first vertical line at $n = 35$, the radius r of the aggregate increases as $n^{1/3}$ in agreement with (1.9), then it falls slightly, and it reaches a constant value after the second vertical line at $n = 48$.

Let us pay attention to the fact that a decrease in r at $n > 35$ for globular aggregates can occur according to eq.(1.10) only with a sufficiently rapid decrease of β_{opt} with increasing n, which is observed in Fig. 3. Constancy of r at $n > 48$ is ensured in accordance with eq.(1.8) by linear growth of λ_{opt} and fixation of β_{opt} as a function of n in Figs. 4 and 3. In Fig. 5, a horizontal line is drawn at $r = 16$ nm, which corresponds to the maximal possible radius of the spherical micelle core, determined by the full length of elongated polar head group of the surfactant molecule $C_{12}E_4$. Note that this limit is not reached in Fig. 5.

According to (1.1), the constant value of the optimal parameter $\beta_{opt} = 0.32748$ in Fig. 3, achieved for spherocylindrical aggregates at $n > 48$, also corresponds to the constant value $\alpha_{opt} = 0.74$ of the parameter α. Note that other constant value $\alpha = 2/3$ was predicted in [14], based on the additional assumption of a constant surface density of surfactants on spherical caps and cylindrical bridge (see Fig. 1). In fact, under this additional condition, we have $n_{sph}/S_{sph} = n_{cyl}/S_{cyl}$ and $V_{sph}/S_{sph} = V_{cyl}/S_{cyl}$. From here, taking into account eqs. (1.3)-(1.6), we obtain a closed equation for β:

$$(2-\beta)(1+\beta) = 3\sqrt{\beta(2-\beta)}\,. \qquad (2.7)$$

The exact root of eq.(2.7), which corresponds to the condition $\beta \le 1$ formulated at the beginning of Section 1, is equal to $\beta = \dfrac{1}{1+\sqrt[3]{2}+1/\sqrt[3]{2}} \simeq 0.32748$, which coincides with the found value of the optimal parameter β_{opt} (see Fig. 3). Accordingly, the corresponding value of the parameter $\alpha = \sqrt{\beta(2-\beta)}$ coincides with $\alpha_{opt} = 0.74$ but not with $\alpha = 2/3$. We can conclude that the optimal values of the parameters β and α are realized for spherocylindrical aggregates at a constant surface density. We emphasize that, calculating the found values $\beta \simeq 0.32748$ and $\alpha = 0.74$, we did not use now the thermodynamic model of the aggregation work, but relied on purely geometric eqs. (1.3)-(1.6) and the additional assumption of a constant surface density of the surfactant molecular groups.

Let us now plot the dependence of the "optimal" work $W_{opt} = W(n,\beta,\lambda,c_{10})\big|_{\lambda=\lambda_{opt}(n),\beta=\beta_{opt}(n)}$ of aggregation of inverse micelles on the aggregation number n. The physical meaning of the "optimal" aggregation work W_{opt} of micelles is that it shows the line of the lowest values of the work $W(n,\beta,\lambda,c_{10})$ when the aggregation number changes, including the saddle point and the

minimum point of $W(n,\beta,\lambda,c_{10})$. This line is shown in Fig. 6 as a solid curve. It is obtained after substituting the optimal expressions for $\lambda_{opt}(n)$ and $\beta_{opt}(n)$ (that satisfy conditions (2.6)) in eq.(2.1) and using the numerical values of the parameters from eq.(2.5).

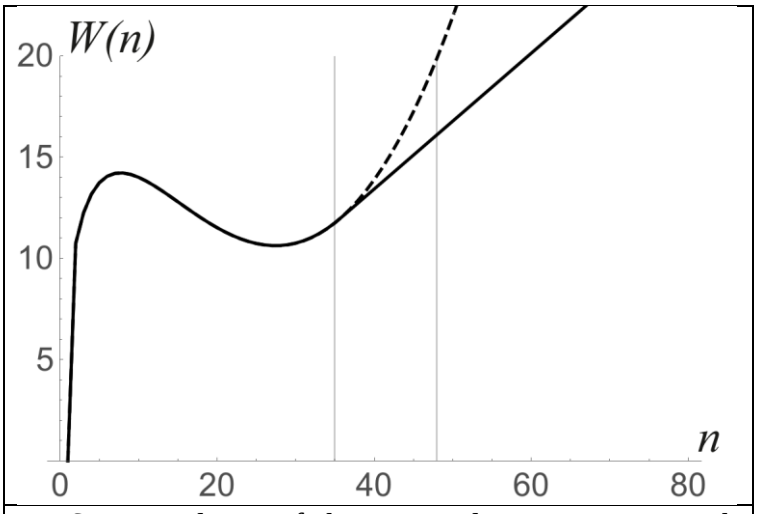

Fig.6. Dependence of the "optimal" aggregation work W_{opt} of inverse micelles of arbitrary form on the aggregation number n in comparison with the aggregation work $W(n,c_{10})$ of inverse spherical micelles.

The dotted line in Fig. 6 shows the dependence of the aggregation work of spherical micelles from Fig.2. The vertical lines in Fig. 6 have the same meaning as in Figs. 3-5: the "optimal" micelle grows up to $n=35$ like a sphere, then changes like a globule in the interval $35<n<48$ and like a spherical cylinder at $n>48$.

We see that the curve of the "optimal" aggregation work of inverse micelles practically coincides with the work of aggregation of inverse spherical micelles at $n<35$, moreover, the saddle point of work $W(n,\beta,\lambda,c_{10})$ coincides with the point of maximum of work W_{opt} and maximum of work $W(n,c_{10})$ at $n=8$, and the minimum of $W(n,\beta,\lambda,c_{10})$ coincides with the minimum of W_{opt} and minimum of work $W(n,c_{10})$ at $n=28$. At $n>48$, the curve of W_{opt} already significantly differs from the aggregation work $W(n,c_{10})$ of spherical micelles, which is associated with the transition of aggregates first into globules, and then into spherocylinders.

3. EQUILIBRIUM DISTRIBUTION OF AGGREGATES AND FLUCTUATIONS OF THE FORM PARAMETERS

The fact that the "optimal" aggregation work W_{opt} of inverse micelles coincides with the work of aggregation of spherical micelles in Fig. 6 at $n<35$ does not at all mean that there are no contributions to the equilibrium distribution of micelles from globular and cylindrical micelles at $n<35$. According to the Boltzmann principle, the expression for the equilibrium distribution ρ of aggregates should have the form

$$\rho(n,\beta,\lambda,c_1)=Ae^{-W(n,\beta,\lambda,c_1)}, \qquad (3.1)$$

where A is the normalization coefficient, which, taking into account the appearance of form parameters, must be determined from additional considerations. For the distribution of spherical micelles in a theory in which the aggregation number is the only variable characterizing the aggregate, one can set $A = c_1$ [7]. It follows from eq.(3.1) that, for any aggregation number $n >> 1$, aggregates can have different forms. Accordingly, we must take into account the fluctuations of the form parameters λ and β. The value of the normalization coefficient A changes in this case.

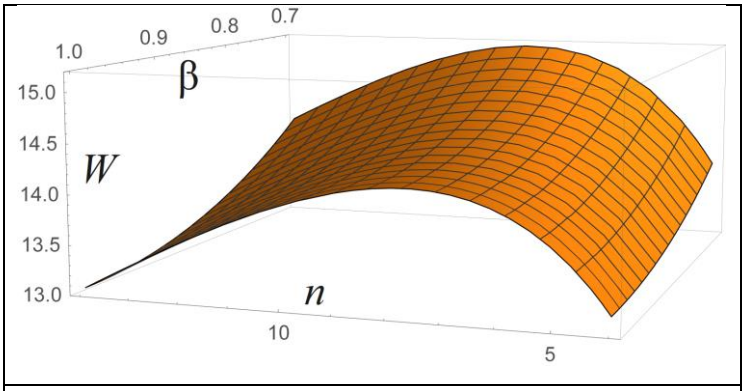

Fig.7. Surface $W = W(n, \beta, \lambda = 0)$ in the vicinity of the saddle point of the aggregation work $W(n, \beta, \lambda, c_{10})$.

Let us study in more detail the aggregation work $W(n, \beta, \lambda, c_{10})$ in two regions: in the vicinity of the saddle point at $5 < n < 15$ and in the region significantly to the right of the minimum of the work at $70 < n < 80$. We begin with the first region. If it is impossible to construct a function of three independent variables in one figure, we will proceed as follows. The prediction of the optimal values of the form parameters gives us at $5 < n < 15$ the values $\lambda_{opt} = 0$ and $\beta_{opt} = 1$, that is, the micelles in this region are predominantly spherical. Since the proportion of spherocylindrical micelles in this region is expectedly small, we can set $\lambda = 0$ and plot the work surface $W(n, \beta, \lambda = 0, c_{10})$ according to eqs.(2.1), (1.3), (1.4) and (1.7), (2.5). This surface is shown in Fig. 7. We see from Fig. 7 that the value $\beta = 1$ is indeed optimal, since it corresponds to the smallest values of the work $W(n, \beta, \lambda = 0, c_{10})$.

Taking into account eq.(3.1), we may define the average value of the parameter β in the vicinity of the saddle point by the relation

$$\langle \beta \rangle = \frac{1}{11} \sum_{n=5}^{15} \frac{\int_{\beta=0}^{1} \beta e^{-W(n,\beta,\lambda=0,c_{10})} d\beta}{\int_{\beta=0}^{1} e^{-W(n,\beta,\lambda=0,c_{10})} d\beta}. \qquad (3.2)$$

Using eqs.(2.1), (1.3), (1.4) and (1.7), (2.5), we find $\langle \beta \rangle = 0.828$. The corresponding standard deviation for β is $\Delta\beta = \sqrt{\left\langle \left(\beta - \langle \beta \rangle \right)^2 \right\rangle} = 0.129$. We see that the average value $\langle \beta \rangle$ is not very

close to 1, and the fluctuations of form parameter β are quite noticeable in the vicinity of the saddle point of the aggregation work. Similarly, considering the average value $\langle\lambda\rangle$ of the parameter λ in the same neighborhood of the saddle point at $\beta_{opt}=1$, we find

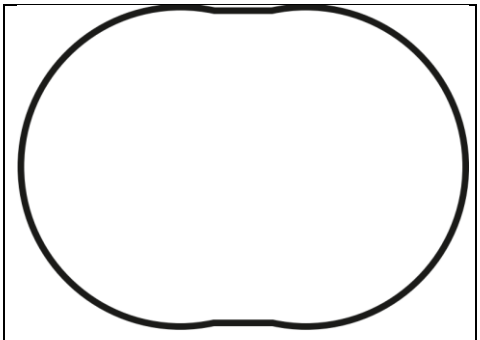

Fig.7a. The shape of the aggregate core at $n=8$, $\langle\beta\rangle=0.828$ and $\langle\lambda\rangle=0.415$.

$$\langle\lambda\rangle=\frac{1}{11}\sum_{n=5}^{15}\frac{\int_{\lambda=0}^{\infty}\lambda e^{-W\left(n,\beta=\beta_{opt}=1,\lambda,c_{10}\right)}d\lambda}{\int_{\lambda=0}^{\infty}e^{-W\left(n,\beta=\beta_{opt}=1,\lambda,c_{10}\right)}d\lambda}=0.415. \qquad (3.3)$$

The corresponding standard deviation for λ is $\Delta\lambda=\sqrt{\left\langle\left(\lambda-\langle\lambda\rangle\right)^2\right\rangle}=0.441$. We see that the average value $\langle\lambda\rangle$ deviates quite noticeably from zero, which would be in the complete absence of spherocylindrical micelles, and the fluctuations of the parameter λ are comparable with its average value. The aggregate core corresponding to the calculated $\langle\beta\rangle$ and $\langle\lambda\rangle$ at $n=8$ is shown in Fig.7a.

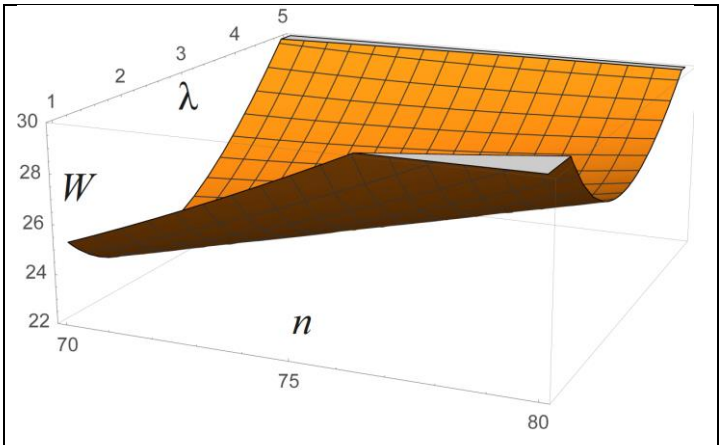

Fig.8. Surface $W=W\left(n,\beta=0.32748,\lambda,c_{10}\right)$ at $70<n<80$.

Consider now the region $70<n<80$ of aggregation numbers. Since spherical and globular micelles are expected to be virtually absent in this region, we set $\beta=0.32748$ and, using eqs.(2.1), (1.3), (1.4) and (1.7), (2.5), plot the surface of work $W=W\left(n,\beta=0.32748,\lambda,c_{10}\right)$. This surface is shown in Fig.8. It is seen that the value λ_{opt}, which corresponds to the "gorge" in Fig. 8, slowly rises along the gorge with the growth of the aggregation number n. Since the average value of the parameter λ will also grow with the growth of n, then we define this value for a certain specific aggregation number $n=75$ by the expression

$$\langle\lambda\rangle=\frac{\int_{\lambda=0}^{\infty}\lambda e^{-W(n=75,\beta=0.32748,\lambda,c_{10})}d\lambda}{\int_{\lambda=0}^{\infty}e^{-W(n=75,\beta=0.32748,\lambda,c_{10})}d\lambda}. \qquad (3.4)$$

Using eqs.(2.1), (1.3), (1.4) and (1.7), (2.5), we find $\langle\lambda\rangle = 2.61$. This average value is close to the optimal value $\lambda_{opt}(n=75) = 2.50$. However, the corresponding standard deviation $\Delta\lambda = \sqrt{\left\langle\left(\lambda - \langle\lambda\rangle\right)^2\right\rangle} = 0.65$ is not small.

Since the value β_{opt} is constant in the interval $70 < n < 80$, then we find the average value $\langle\beta\rangle$ of the parameter β at $\lambda_{opt}(n=75) = 2.50$ with the help of formula

$$\langle\beta\rangle = \frac{1}{11}\sum_{n=70}^{80} \frac{\int_{\beta=0}^{1} \beta e^{-W\left(n,\beta,\lambda=\lambda_{opt}(n),c_{10}\right)} d\beta}{\int_{\beta=0}^{1} e^{-W\left(n,\beta,\lambda=\lambda_{opt}(n),c_{10}\right)} d\beta} = 0.332. \tag{3.5}$$

This value is close to the optimal value $\beta_{opt}(n=75) = 0.327$. The corresponding standard deviation $\Delta\beta = \sqrt{\left\langle\left(\beta - \langle\beta\rangle\right)^2\right\rangle} = 0.049$ is not large.

Let us define the integral aggregation work $W_{int}\left(n, c_1\right)$ as follows:

$$W_{int}\left(n, c_1\right) = \begin{cases} -\ln\left(A\int_0^1 d\beta \int_0^\infty d\lambda e^{-W(n,\beta,\lambda,c_1)} \right), & n > 1 \\ 0, & n = 1. \end{cases} \tag{3.6}$$

As follows from eqs.(3.1) and (3.6), the value $e^{-W_{int}(n,c_1)}$ determines the concentration of surfactant aggregates of any form with the given aggregation number n. This allows us to solve the problem of the normalization factor A by requiring in the region of initial spherical aggregates (for example, in the range $1 \le n \le 5$) the equality

$$A\int_0^1 d\beta \int_0^\infty d\lambda e^{-W(n,\beta,\lambda,c_1)} = c_1 e^{-W(n,c_1)}. \tag{3.7}$$

Figure 9 shows the dependences of the integral aggregation work $W_{int}\left(n, c_1\right)$ on the aggregation number n in comparison with the work $W\left(n, c_1\right)$ of aggregation of spherical inverse micelles, plotted according to eqs.(3.6), (2.2) with using eqs.(2.1), (1.3), (1.4) and (1.7), (2.5) at two concentrations of surfactant monomers. The normalization parameter in accordance with (3.7) was set to $A = 8$.

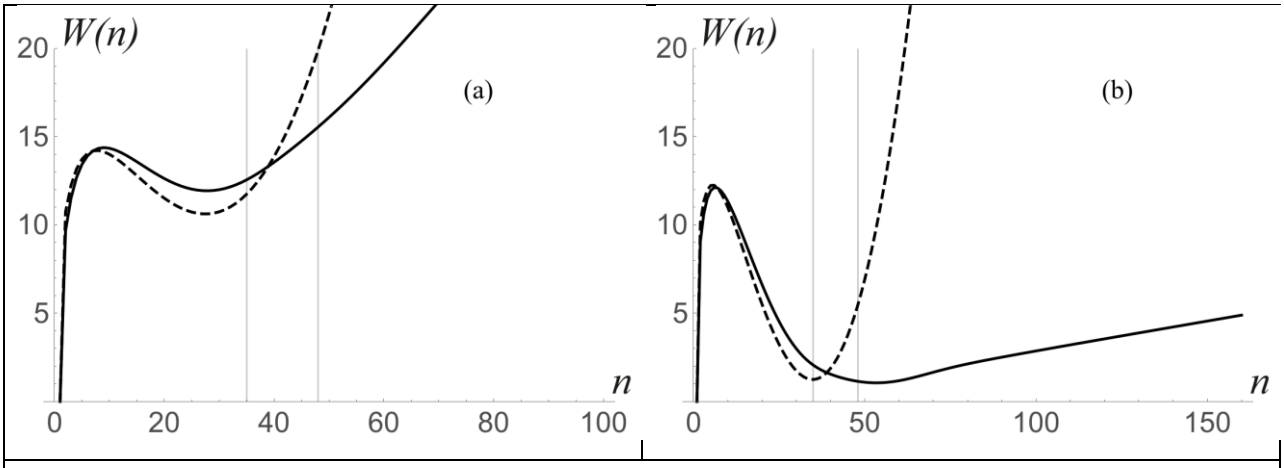

Fig.9. Dependence of the integral aggregation work $W_{\text{int}}(n,c_1)$ on the aggregation number n at $A=8$ (solid line), as well as the aggregation work $W(n,c_1)$ of inverse spherical micelles (dashed line) at the monomer concentration $c_{10}=1.35\times10^{22}$ m^{-3} (left figure (a)) and concentration $c_1=1.35c_{10}$ (right figure (b)).

4. THE DEGREES OF MICELLIZATION IN THE PRESENCE OF MICELLES OF DIFFERENT FORM

Knowing the expression (3.1) for the equilibrium distribution ρ of aggregates as a function of n, β, λ and the normalization coefficient A, we can describe the fractions of surfactants in micelles of different forms at different concentrations of surfactant monomers. Aggregates with small aggregation numbers n and noticeably fluctuating parameters β and λ (see Fig. 7a) are practically impossible to identify as spheres, globules, or spherocylinders; therefore, in what follows, it is reasonable to speak about short and long micelles. We will call aggregates long micelles, in which $\lambda\geq2\beta$, that is, the total length of micelles is at least $4r$, and short aggregates are all the rest.

For a given surfactant monomer concentration c_1, we introduce the following definitions:

$$\alpha_{\text{sm}}\equiv\frac{A\int_{n_c}^{\infty}dn\int_0^1 d\beta\int_0^{2\beta}d\lambda n e^{-W(n,\beta,\lambda,c_1)}}{c_1+A\int_{n_c}^{\infty}dn\int_0^1 d\beta\int_0^{2\beta}d\lambda n e^{-W(n,\beta,\lambda,c_1)}}, \tag{4.1}$$

$$\alpha_{\text{lm}}\equiv\frac{A\int_{n_s}^{\infty}dn\int_0^1 d\beta\int_{2\beta}^{\infty}d\lambda n e^{-W(n,\beta,\lambda,c_1)}}{c_1+A\int_{n_c}^{\infty}dn\int_0^1 d\beta\int_0^{\infty}d\lambda n e^{-W(n,\beta,\lambda,c_1)}}, \tag{4.2}$$

$$\alpha_f \equiv \frac{A\int_{n_s}^{\infty} dn \int_0^1 d\beta \int_0^{\infty} d\lambda n e^{-W(n,\beta,\lambda,c_1)}}{c_1 + A\int_{n_c}^{\infty} dn \int_0^1 d\beta \int_0^{\infty} d\lambda n e^{-W(n,\beta,\lambda,c_1)}}, \qquad (4.3)$$

where α_{sm} is the degree of micellization in short micelles, α_{lm} is the degree of micellization in long micelles, and α_f is the degree of micellization in micelles of any form and length. Since $c_1 + A\int_{n_c}^{\infty} dn \int_0^1 d\beta \int_0^{\infty} d\lambda n e^{-W(n,\beta,\lambda,c_1)}$ is a total concentration of surfactants in unit volume of the solution, α_{sm} characterizes the fraction of surfactant molecules in short micelles at a given total surfactant concentration and α_{lm} sets the corresponding fraction of surfactant molecules in long micelles. Obviously, $\alpha_f = \alpha_{sm} + \alpha_{lm}$.

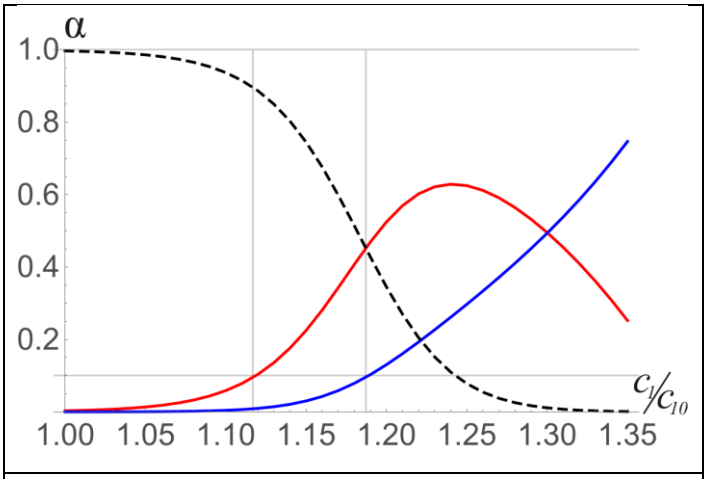

Fig.10. The degree α_{sm} of micellization in short micelles (red line), the degree α_{lm} of micellization in long micelles (blue line) and the relative fraction of surfactants in the form of monomers (dotted line) as a function of c_1/c_{10}.

Figure 10 shows the curves of dependence of the micellization degrees α_{sm}, α_{lm} and the fraction $1-\alpha_{sm}-\alpha_{lm}$ of surfactant monomers per unit volume of the solution as a function of the equilibrium concentration c_1 of surfactant monomers. These curves are plotted with the help of eqs. (4.1) and (4.2) with using eqs.(3.1), (2.1), (1.3), (1.4) and (1.7), (2.5) at $A = 8$. The thin lines show the concentrations c_1 at which micellization degrees α_{sm} and α_{lm} reach the values $\alpha_{sm} = 0.1$ (at $c_1 = 1.117 c_{10}$) and $\alpha_{lm} = 0.1$ (at $c_1 = 1.187 c_{10}$). These values correspond to the total concentration of surfactants in the solution at the first and second CMC, respectively. Figure 10 shows that these total surfactant concentrations are spaced on the axis of monomer concentrations and are actually described in terms of the proposed molecular thermodynamic model. It is seen that between the first and second CMC, surfactant is accumulated in short micelles, but above the second CMC, the relative fraction of the substance in short micelles passes through a maximum and then rapidly decreases compared to the fraction of surfactant in long micelles.

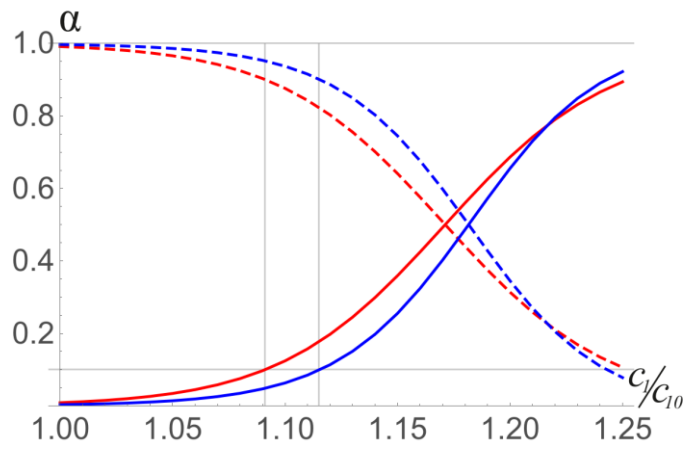

Fig.11. Dependences on c_1/c_{10} for the micellization degree α_{sph} in spherical micelles (red line) in one-dimensional theory, the total micellization degree α_f in micelles of any form (blue line) in three-dimensional theory, the relative fraction of surfactants in the form of monomers when there are only spherical micelles (red dotted line) and micelles of any form (blue dotted line).

To illustrate the role of fluctuations of form parameters, Fig. 11 shows the dependence on c_1 for the degree of micellization for spherical inverse micelles $\alpha_{sph} = \int_{n_c}^{\infty} dnne^{-W(n,c_1)} \left(1+\int_{n_c}^{\infty} dnne^{-W(n,c_1)}\right)^{-1}$, plotted with the one-dimensional distribution $\rho(n,c_1) = c_1 e^{-W(n,c_1)}$, and the dependence on c_1 for α_f plotted according to eq.(4.3). The fact that the curve α_f grows with c_1 at first more slowly than the curve α_{sph}, and then becomes ahead of it, is in agreement with the behavior of the curves of the integral aggregation work $W_{int}(n,c_1)$ in Fig.9.

CONCLUSIONS

In this communication, a new statistical thermodynamic model of inverse non-ionic aggregates of surfactant molecules in non-polar solvents is substantiated. The model allows fluctuation coexistence of spherical, globular, and spherocylindrical aggregates without activation barriers between them. It is shown that for any aggregation numbers in this model, the work of aggregation depends not only on the aggregation numbers and the concentration of surfactant monomers, but also on the parameters characterizing the deviation from the spherical form of the aggregate towards globular and spherocylindrical aggregates. A method for estimating the normalization factor for the distribution of aggregates by aggregation numbers and form parameters is proposed, which makes it possible to find the degree of micellization of a surfactant solution in the presence of micelles of different forms. It is shown that the optimal values of the form parameters, which minimize the work of aggregation, are in good agreement for spherocylindrical aggregates with the predictions of a purely geometric model of such aggregates under the additional assumption of a uniform surface density of molecular groups on the micelle core. The considered molecular thermodynamic model can be extended to direct micelles.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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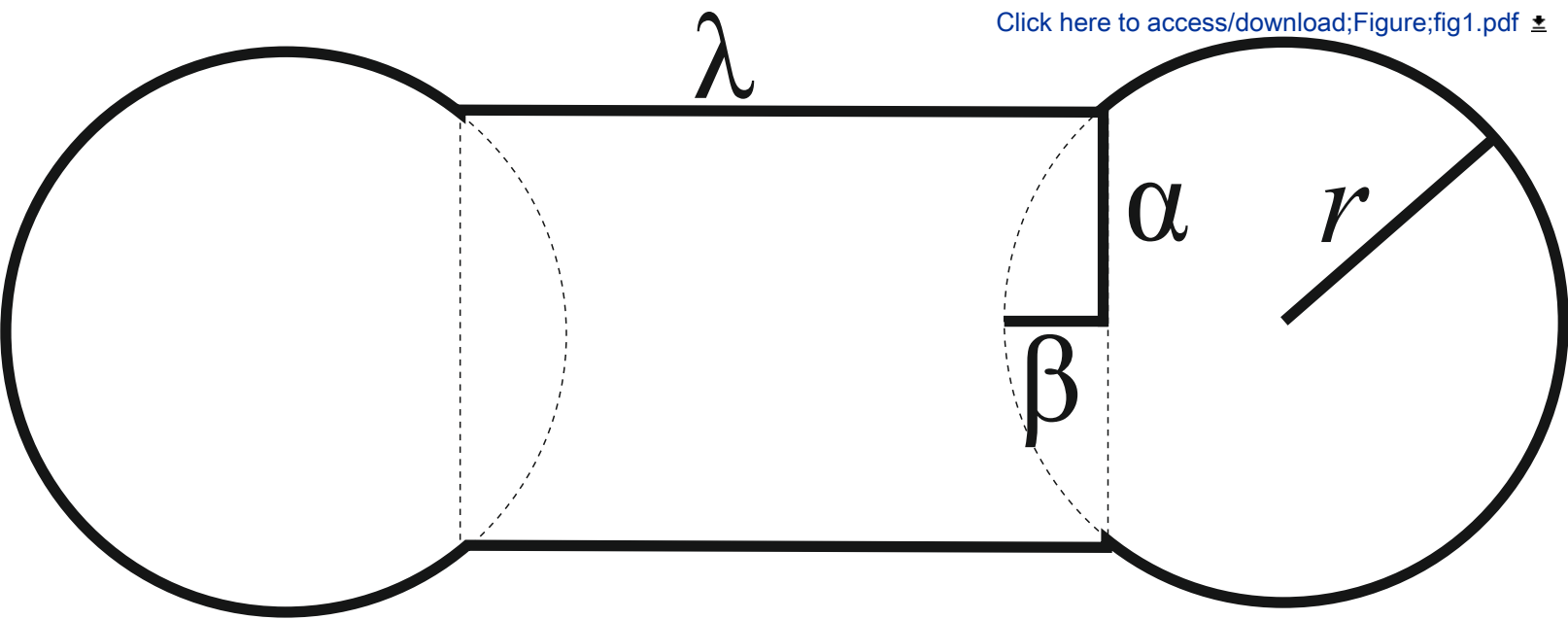

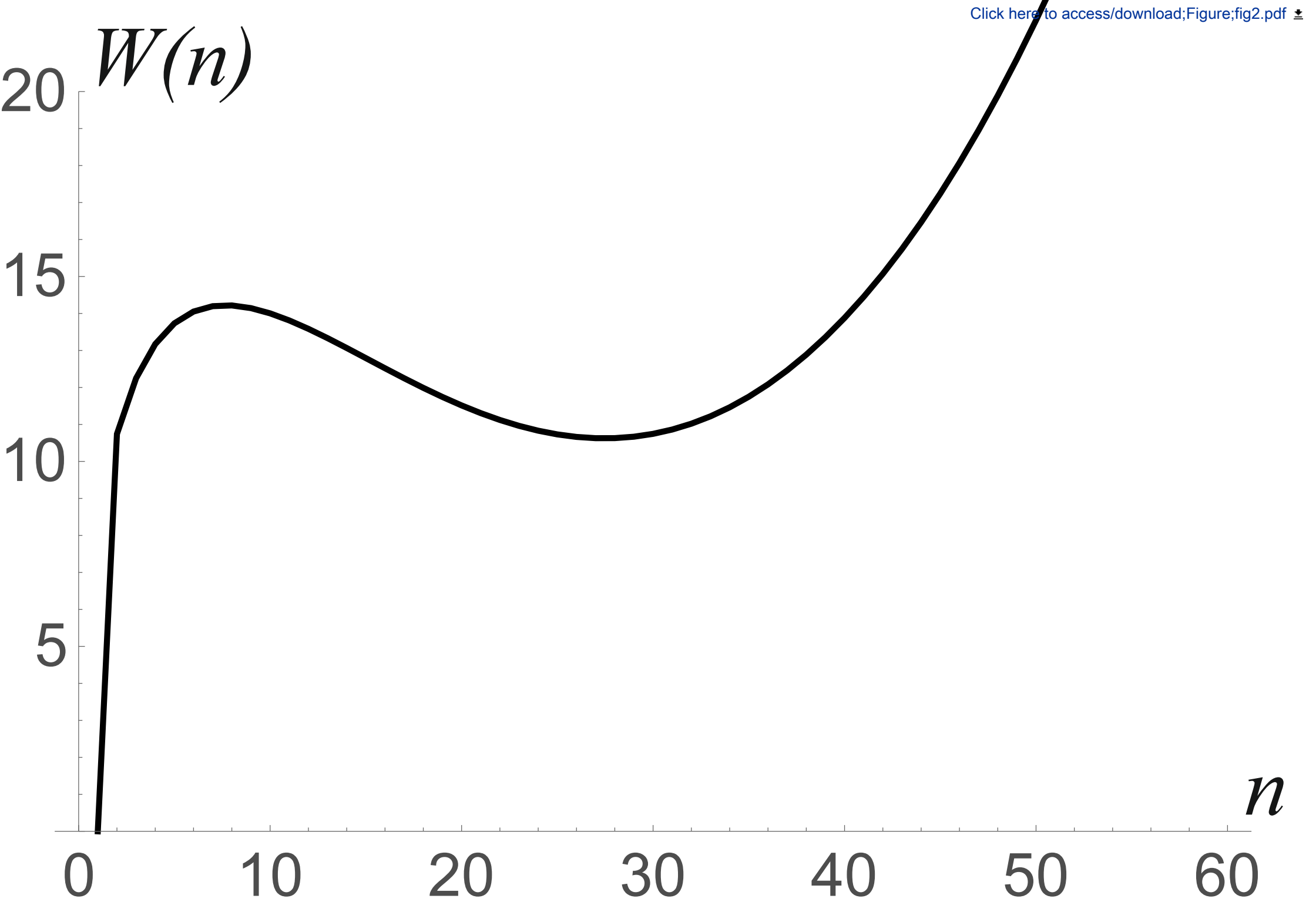

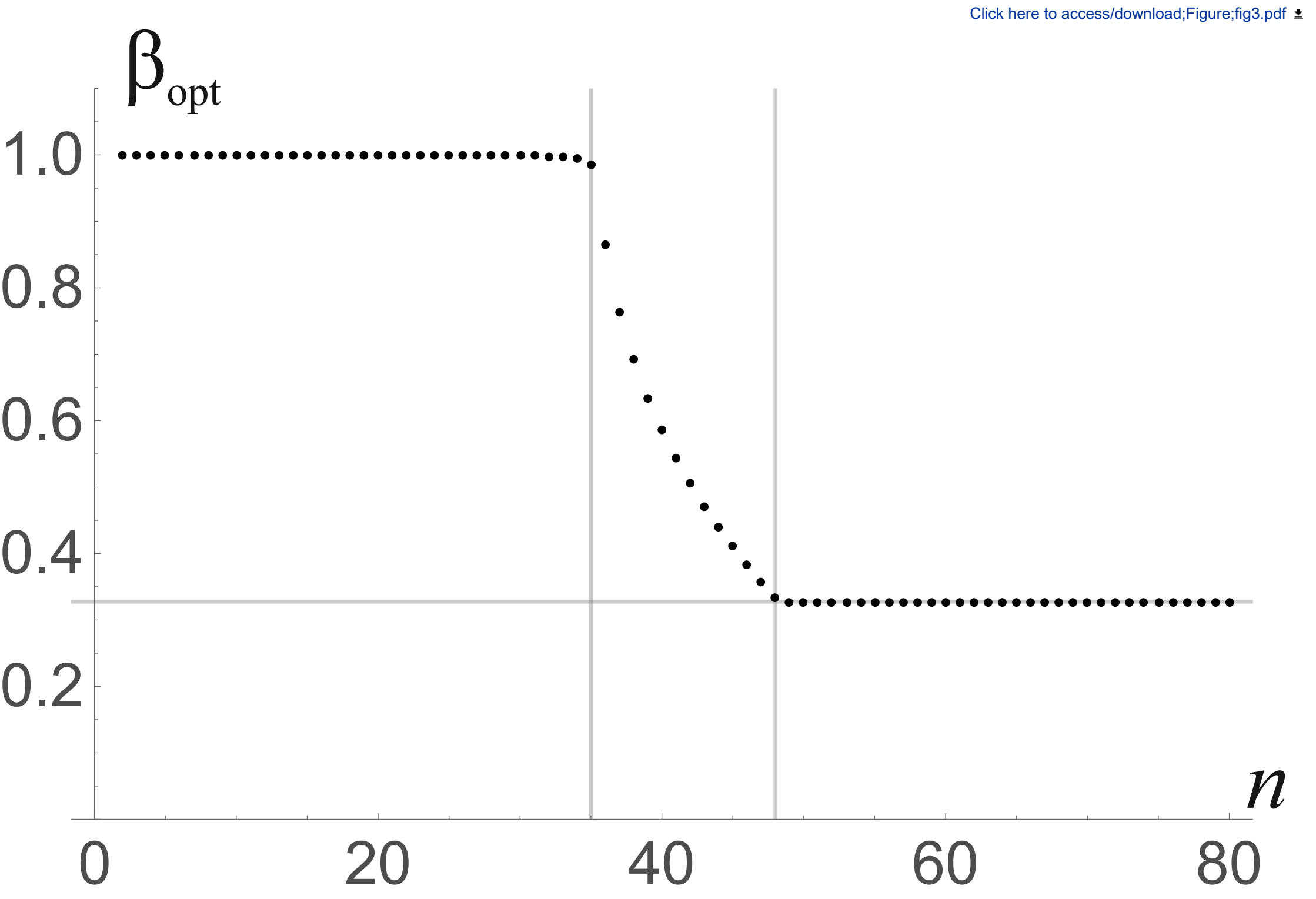

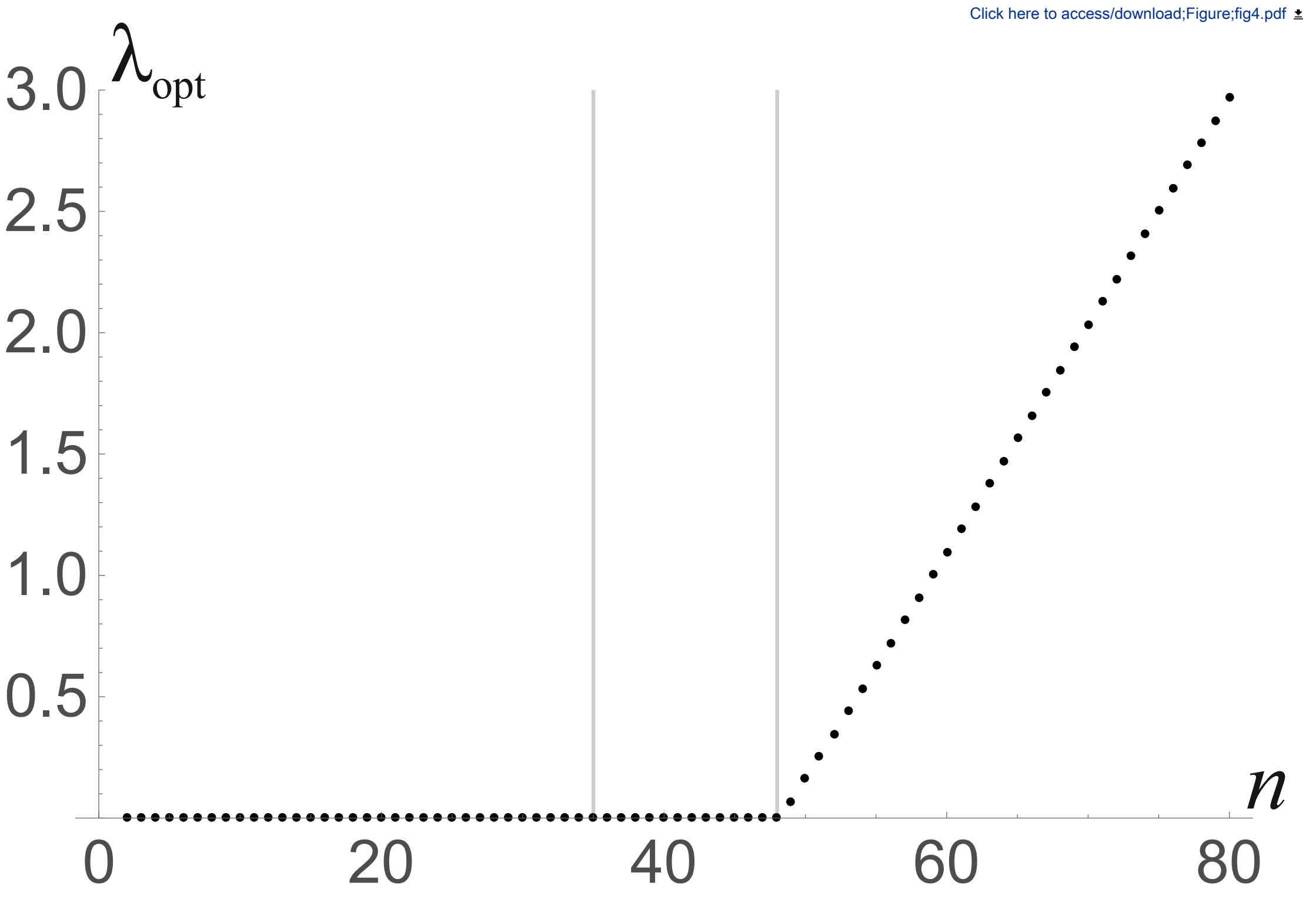

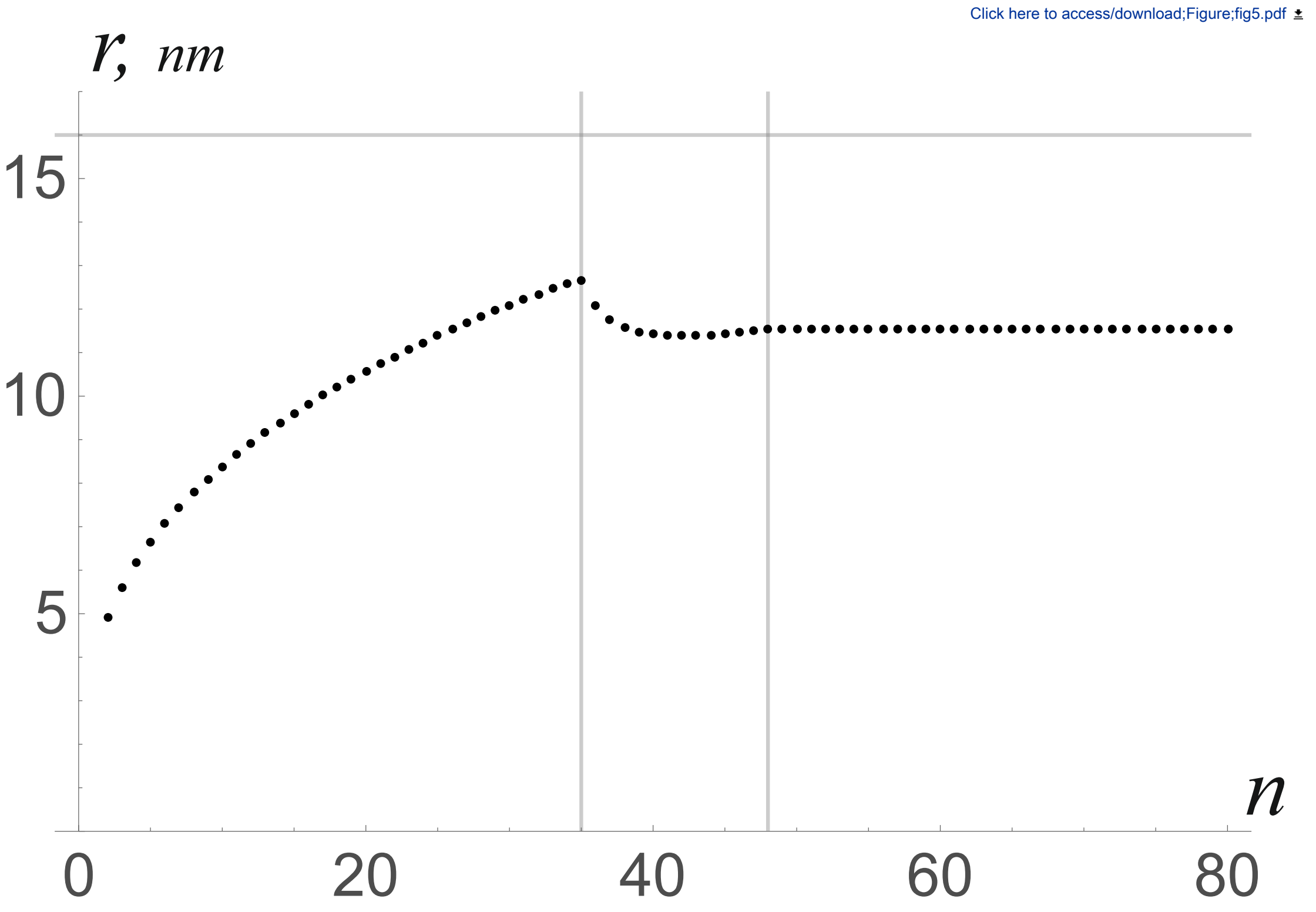

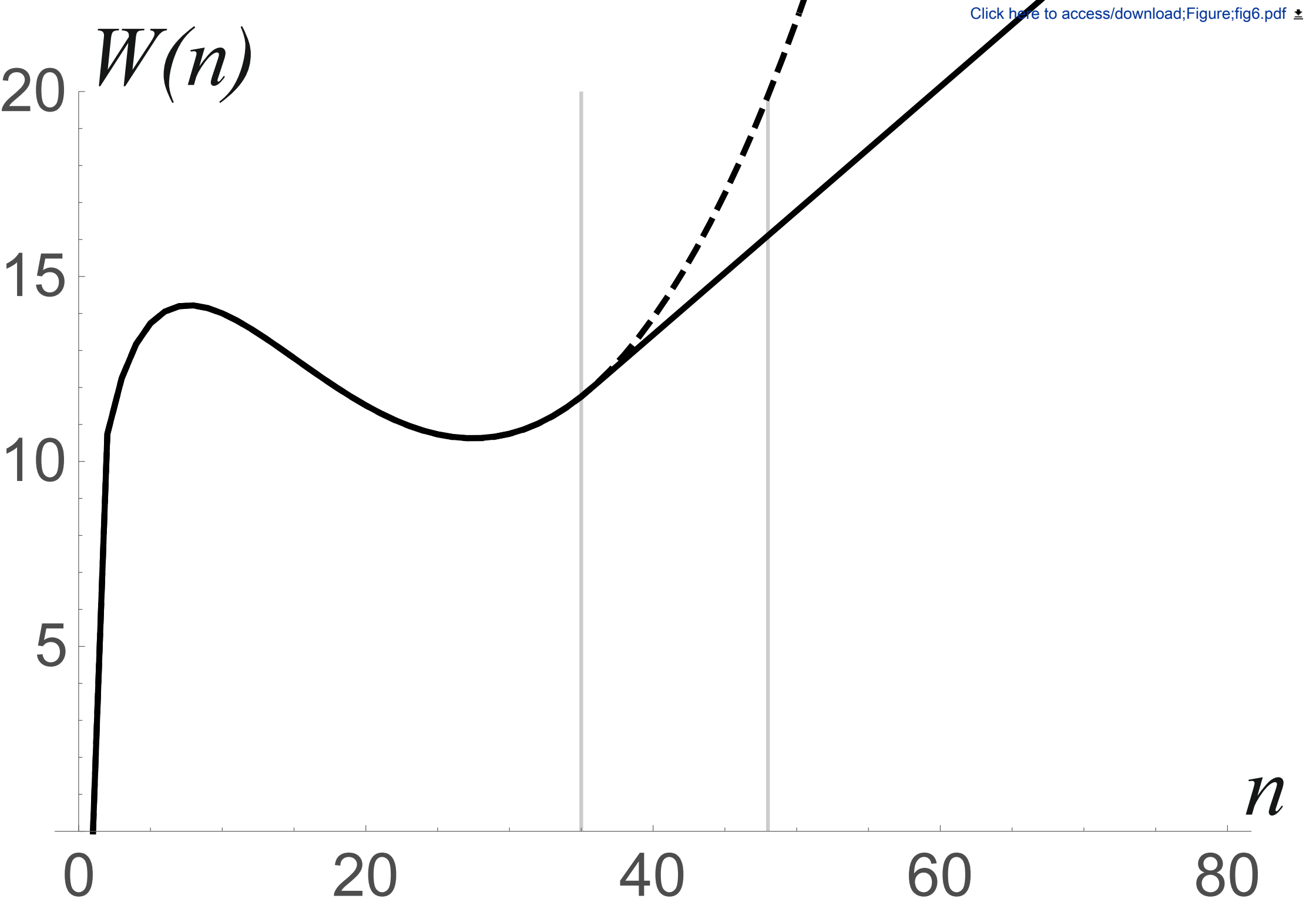

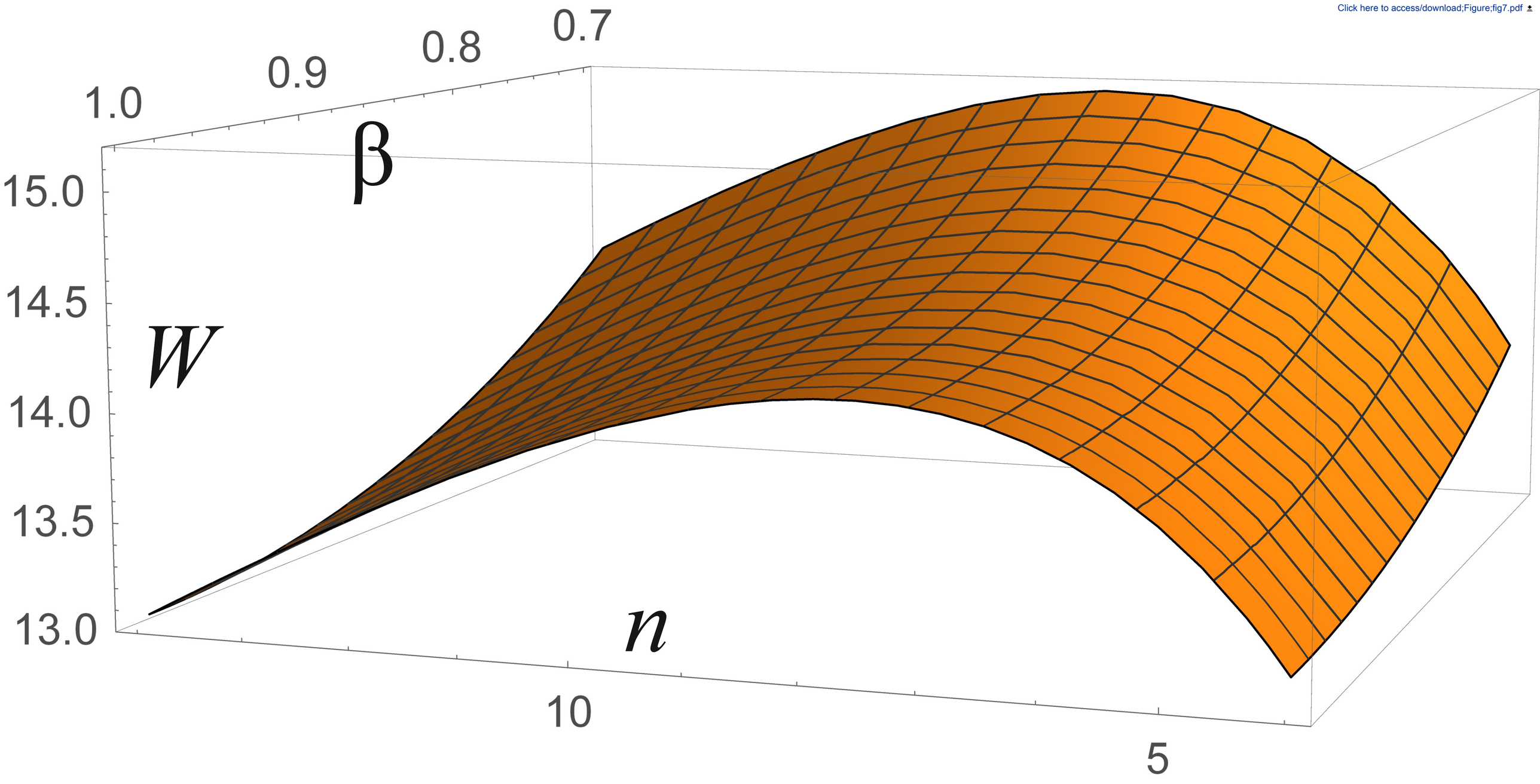

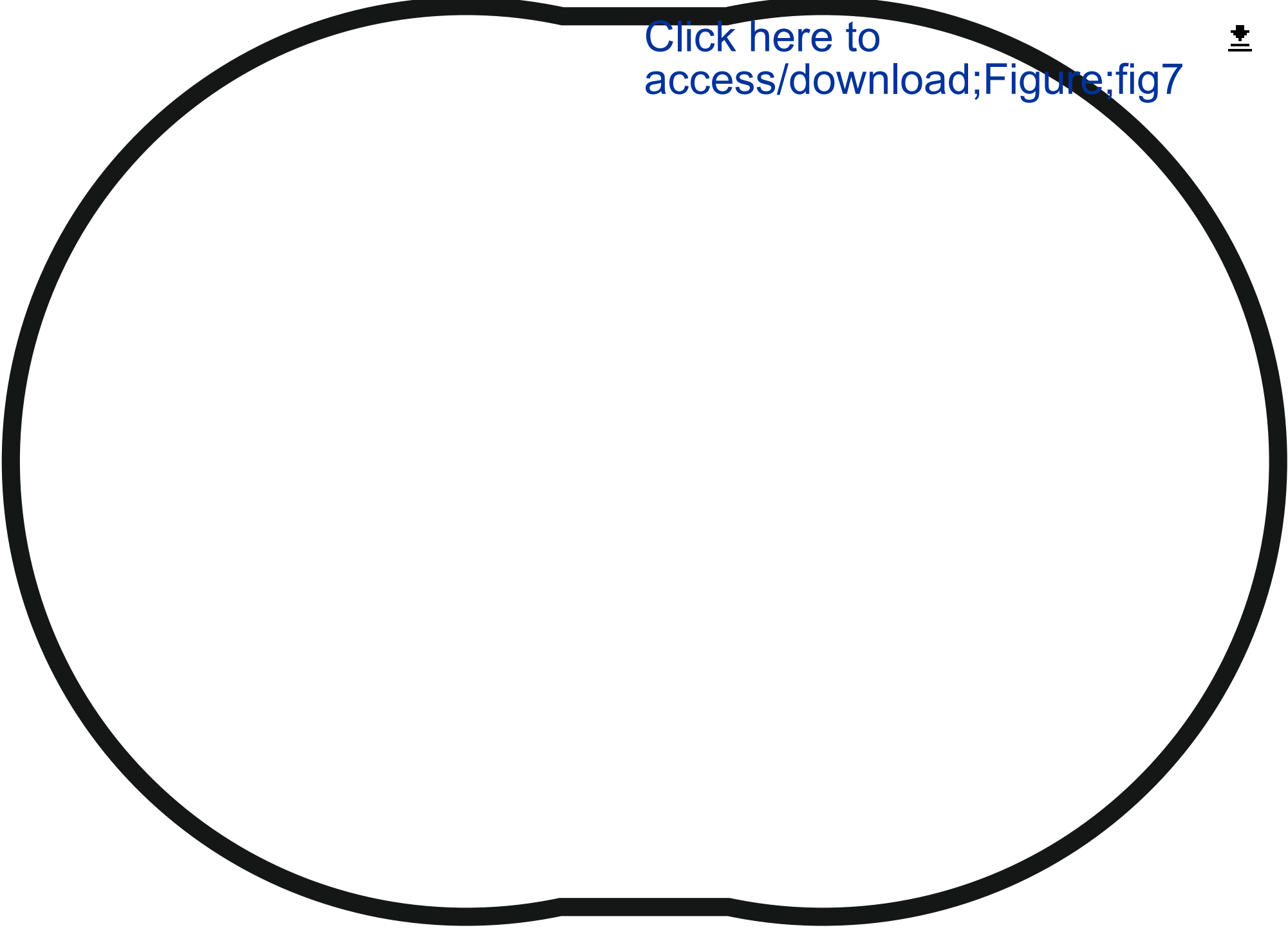

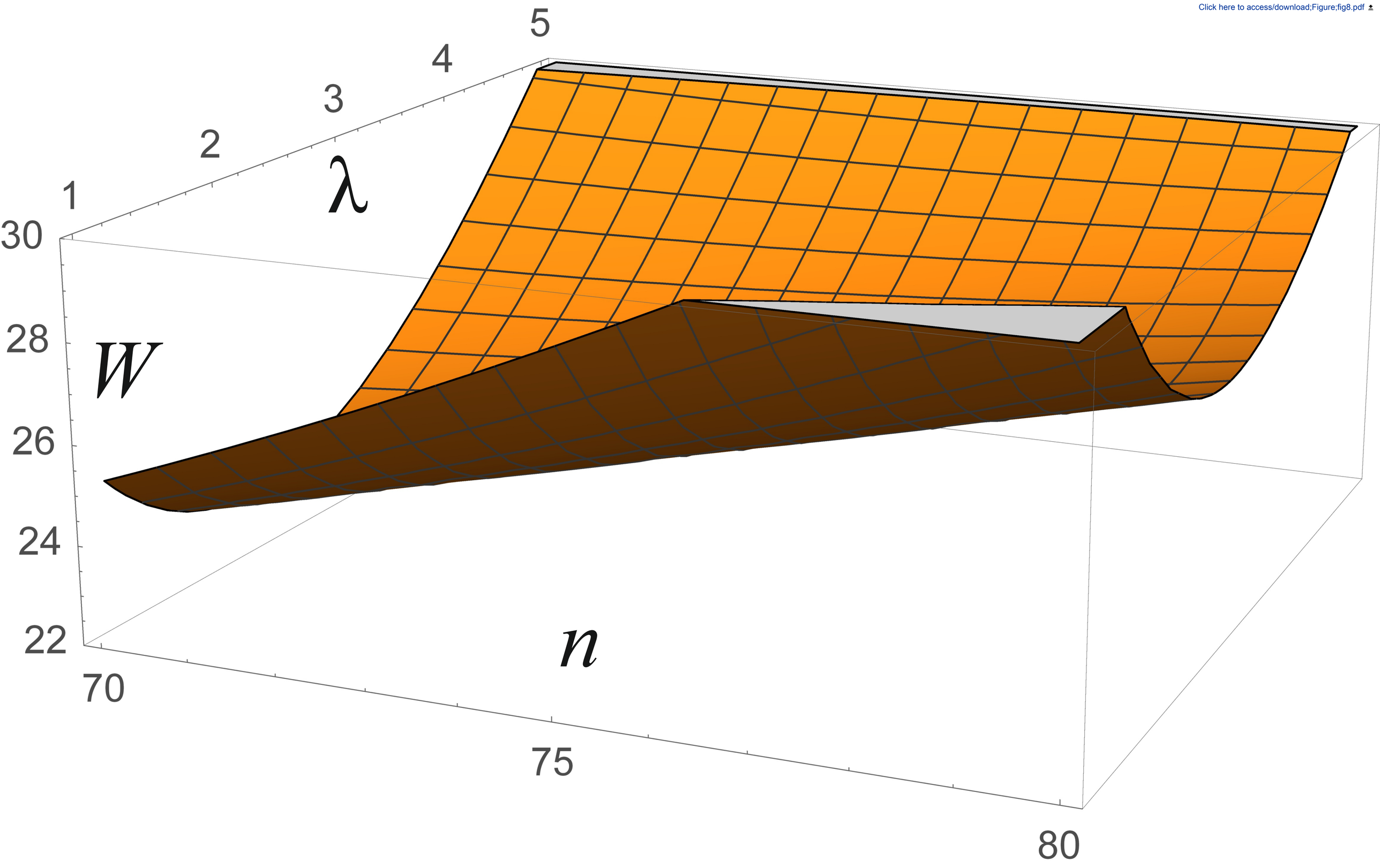

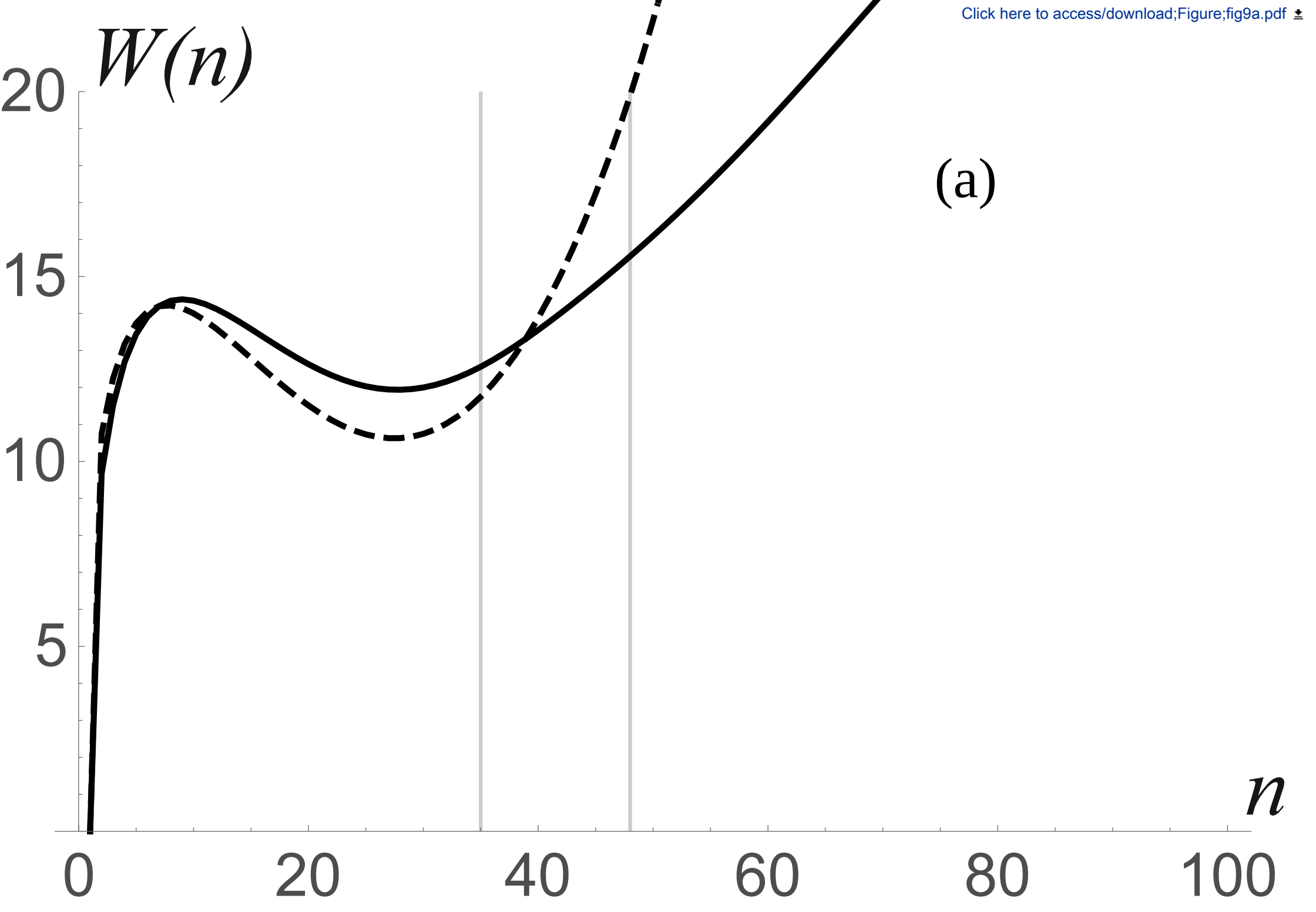

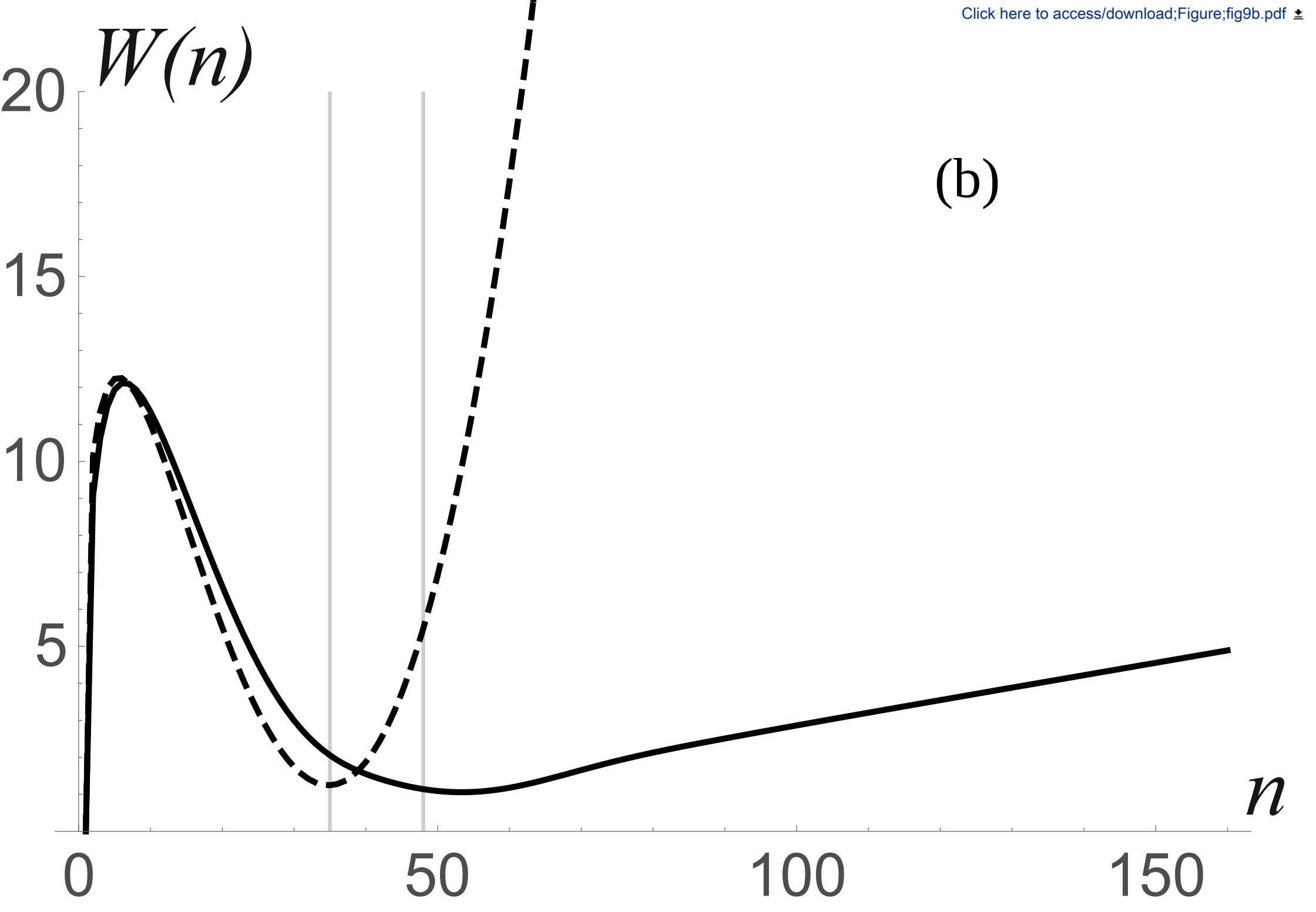

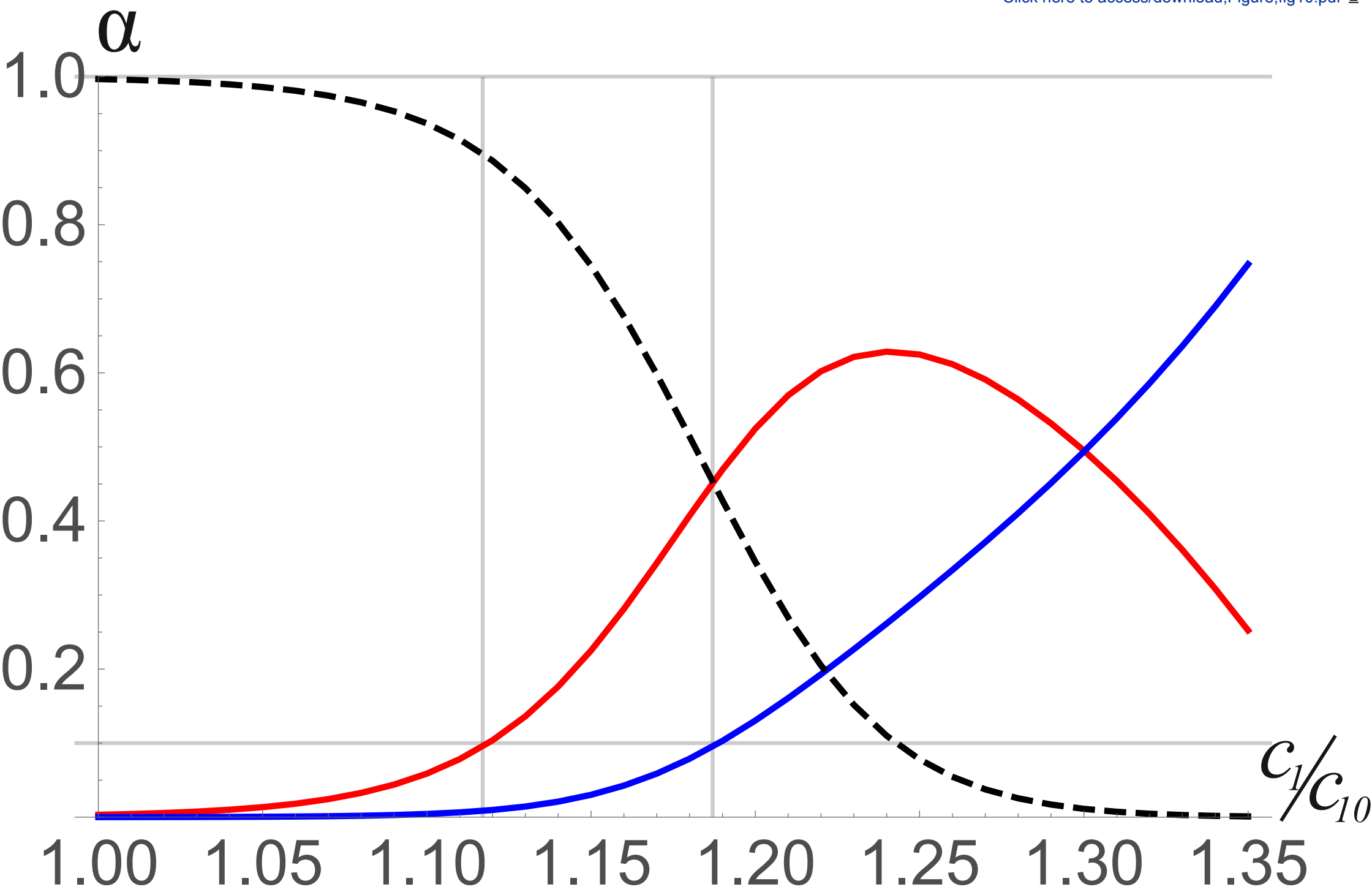

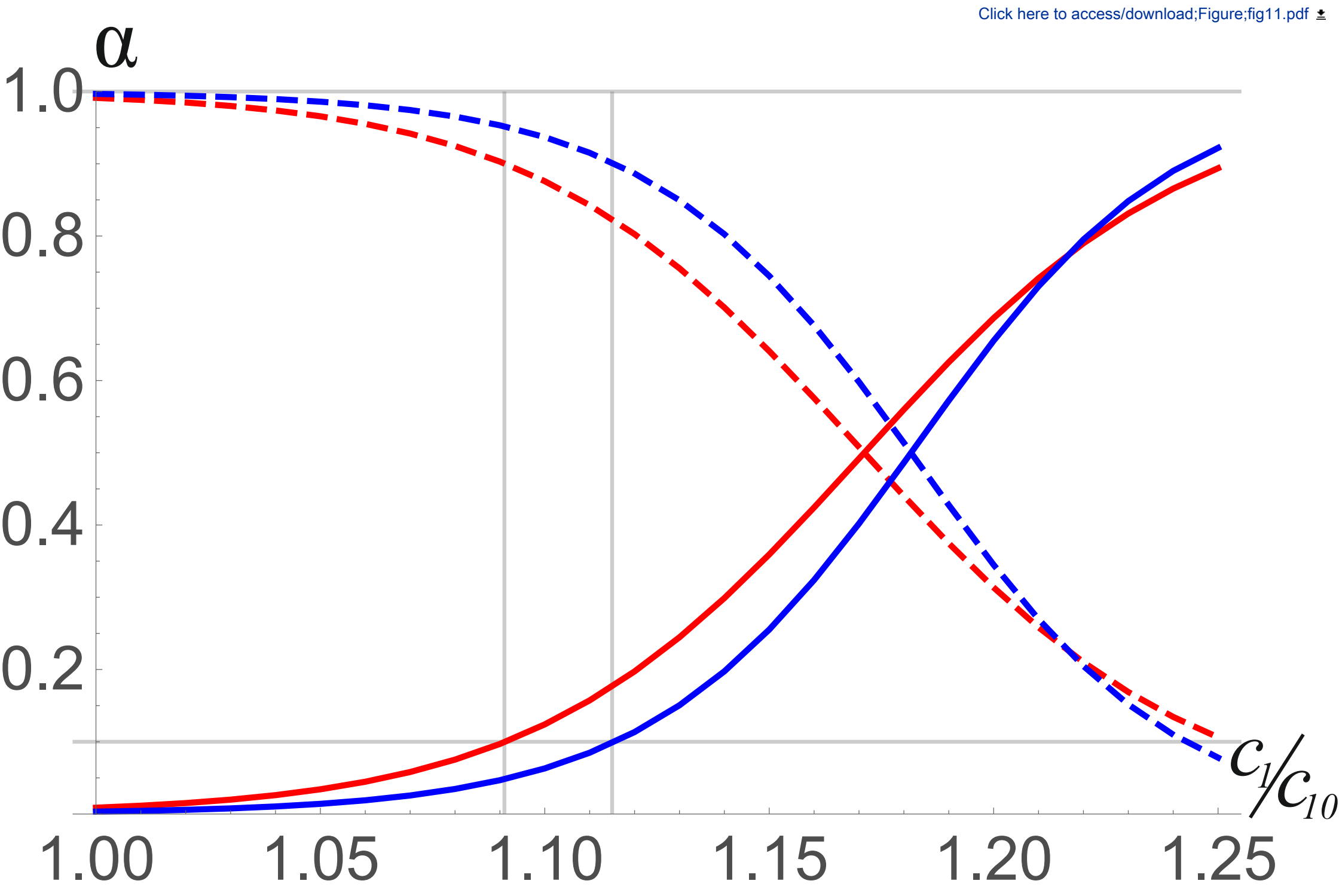

Declaration of interests

☐The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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