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Polymer Chain Size from Geodesic Path and Geometrical Bolyai–Lobachevskij Partition Function. Application to Swelling of Macromolecules in Solution and Micellar Growth

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The Bolyai–Lobachevskij (BL) formula, relating parallelism angle and distance in a Non-Euclidean space, is used to introduce a geometrical partition function. Employing a correspondence between Boltzmann factor and BL characteristic length, allows us to get a simple relation for average size and space curvature, which is the analogy to the equation for the mean energy derived from the ordinary partition function. Due to the equivalence, recently proposed, between a chain molecule in a liquid and a geodesic path in a relativistic space, the equation obtained is expected to be suitable for describing geometrical phenomena in polymer-like networks. Simple applications to swelling of polymer solutions and micellar growth are presented and discussed.

KEY WORDS: Geometrical partition function; Bolyai–Lobachevsky formula; Geodesic path; polymer chain size.

INTRODUCTION

The roles played by topology in quantum mechanics, field theory and polymer physics are of great importance, and closely related to each others.(1) For instance, the Aharonov–Bohm quantum effect has its anology in the statistics of planar Brownian walks in the presence of a hole,(2) while it has been pointed out that polymer representation has a remarkable role in gravity.(3) Basically, topological constraints in polymer systems can be seen as restrictions to the phase space originally available, as determined

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by uncrossability of real chain molecules, and have been tackled successfully according to the famous reptation and universality concepts.(4)

More recently,(5) scaling laws for ideal and real macromolecular chains have been derived by regarding a simple liquid as a (weak) relativistic continuum. A change in the diffusion coefficient, caused by a macromolecule that replaces N liquid units, results in a space curvature which can be dealt with as a perturbation to the pure Euclidean (the so-called Minkowskian) metric for the flat space.(6) To model concentrated polymer solutions, we took then advantage of the so-called Principle of Equivalence,(7) stating that it is always possible to find a reference system where the law of motion (here, of diffusion) take the same form as it would be within an ordinary Euclidean space. In this way, the chain-in-a-tube becomes representative of a geodesic path, i.e., the shortest (o longest) path between two spacetime events, end-to-end distance being measured by the proper time.(4–7)

In this paper, to describe the spatial part of a geodesic curve, the Bolyai–Lobachevskij (hereinafter BL) law is applied to build up a geometrical partition function. A correspondence set for Boltmann factor and BL constant, enables us to get the chain size as a function of the space curvature. Such a result further supports a possible geometrical formulation of statistical thermodynamics, recently proposed through a new scaling concept for geometry.(8) In the last section, the relationship achieved is employed to model swelling of polymer solutions and micellar growth.

THEORETICAL SECTION

Literature on Non-Euclidean geometry starts in 1829,(9) with studies by N. Lobachevskij, who calculated the natural unit of distance definable in a Non-Euclidean space. Consider the right triangle of Fig. 1, provided

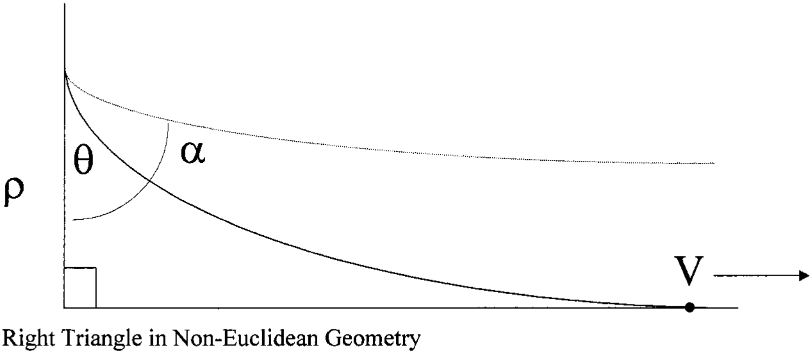

Fig. 1. Graphical illustration of unit of distance in a Non-Euclidean space and BL formula.

with fixed edge $\bar{\varrho}$. When the vertex V is moving infinitely far away, the angle θ increases up to a limit value that must be less than a right angle, $\alpha < \pi/2$. He proved that[10] $\bar{\varrho} = -\ln \tan(\alpha/2)$. Afterwards, the BL formula[10] provided a generalization of this achievement by relating the parallelism angle (α) to the distance (ϱ) through a characteristic length value (L). It is one of the most remarkable equations in all of mathematics, and is usually written as:

$$\exp\left(-\frac{\varrho}{L}\right) = \tan\frac{\alpha}{2} \tag{1}$$

Originally, Lobachevskij used the notation $\alpha = \alpha(\varrho)$ to indicate the parallelism angle at the distance ϱ. In ordinary geometry, one constantly has $\alpha = \pi/2$. In a Non-Euclidean space, the parallelism angle depends instead upon distance and BL length. L, which may in turn be depending on ϱ, specifies the space curvature[11, 12] and, from Eq. (1), one gets two limit conditions:

$$\lim_{L \to l} \alpha(\varrho) = \begin{cases} \pi/2 & l = \infty \\ 0 & l = 0 \end{cases} \tag{2}$$

The first case corresponds to ordinary geometry, whereas the second condition points out a space where the parallelism angle is always zero (say, a space with maximum hyperbolicity). It is worth noting that in a geometry which is physically real, the characteristic length is extremely large,[13] but can never be set to $L = \infty$.

This paper deal with applications of the BL formula to investigate some simple geometrical properties of polymers in solution. The equivalence between macromolecules in a liquid and metric transformations in a relativistic Brownian space enables us to use Eq. (1). One has only to remind that α and ϱ account for the polymer chain curvature implied by a given L value. BL length is then expected to depend upon physical quantities that govern diffusion of macromolecules. However, Eq. (1) alone is not sufficient to get a description of a polymer system. It should somewhat take into consideration statistics of chain displacement lengths, and therefore be completed through other equations. One effective way to do so is certainly employing the partition function concept and combining BL formula and Boltzmann probability, which are both involving exponential terms. We only need to state some correspondence between Boltzmann factor and BL constant, as supported by a recent geometrical formulation of statistical thermodynamics.[8]

Let $Z_\beta = \sum e^{-\beta\varepsilon}$ be the ordinary partition function,(14) where ε_k is the energy of the kth state and $\beta = 1/k_B T$ is the inverse of the Boltzmann constant k_B times the absolute temperature T. Comparing the Boltzmann probability to the left side of Eq. (1), setting $\varepsilon \equiv \Lambda\varrho$ and introducing an average BL length(15) $\bar{L}$, allow us to write:

$$\varepsilon \simeq \bar{\Lambda}\varrho \tag{3}$$

where $\bar{\Lambda} = k_B T/\bar{L}$ has the dimension of an energy per unit length. Equation (3) identifies a partition function (Z_λ) based on the geometrical features of the space according to Eq. (1). For a system characterized by a discrete length distribution, say $\{\varrho_j\}$, we have:

$$Z_\lambda = \sum_j e^{-\varrho_j/\bar{L}} \tag{4}$$

and, in a continuous domain:

$$Z_\lambda = \int_0^\infty \zeta(r)\, e^{-r/\bar{L}}\, dr \tag{5}$$

where $\zeta = \zeta(r)$ is the state density as a function of the radial coordinate.(16) Since $1/\bar{L}$ is the analogy to β, let $\bar{\varrho} \equiv \sqrt{\bar{\varrho}^2}$, Eqs. (4)–(5) lead to:(14, 16)

$$\frac{\bar{\varrho}}{\bar{L}} = \left(\frac{\partial \ln Z_\lambda}{\partial \ln \bar{L}}\right) \tag{6}$$

which stands for the well-known law $\bar{\varepsilon} = -(\partial \ln Z_\beta/\partial\beta)$, provided $\varepsilon \Rightarrow \varrho$ and $\beta \Rightarrow 1/\bar{L}$. In the Appendix, two simple calculations are done when (i) a normal distribution, with fixed root mean square σ, and (ii) an exponential distribution, with average length $\mathscr{L}$, are considered. Adopting(17) $\zeta(r) \propto e^{-r^2/\pi\sigma^2}$, the first case implies:

$$a(x) = \frac{e^{-x^2}}{1 - \Phi(x)} - \pi^{1/2}x \tag{7}$$

with $a = \bar{\varrho}/\sigma$ and $x = \pi^{1/2}\sigma/2\bar{L}$, and where $\Phi = \Phi(x)$ denotes the so-called probability (or error) integral. In (ii), let(17) $\zeta(r) \propto e^{-r/\mathscr{L}}$ (say, a micellar system(18)) one obtains:

$$b(y) = (1 + y)^{-1} \tag{8}$$

where $b = \bar{\varrho}/\mathscr{L}$ and $y = \mathscr{L}/\bar{L}$ are conceptually equivalent to a and x in Eq. (7). More generally, when $\zeta(r) \propto r^{\nu-1}e^{-r/\mathscr{L}}$ and $\nu \in \Re^{+}$, it can be proved (see the Appendix) that Eq. (5) holds with $b = \bar{\varrho}/\nu\mathscr{L}$.

In the next section, we will discuss and apply Eqs. (7)–(8) to experimental data, concerning (i) swelling of polymer networks and (ii) micellar growth.

RESULTS AND DISCUSSION

In (i), Eq. (7) gives the ratio between the average arc lengths of two geodesic curves, i.e., Non-Euclidean ($\bar{\varrho}$) and Euclidean (σ) respectively, and admits two limit conditions:

$$\lim_{\bar{L} \to l} a(x) = \begin{cases} 1 & l = \infty \\ \infty & l = 0 \end{cases} \tag{9}$$

If an Euclidean space is considered, $a = 1$ returns the average size definition, $\bar{\varrho} = \sigma$. On the other hand, in the limit of $\bar{L} \to 0$, a divergent arc length (and ratio, if σ is fixed to a constant value) is expected. We are thus led to the sketch of Fig. 2, depicting schematically the increase of the geodesic path with increasing average curvature (i.e., with decreasing $\bar{L}$ values). Observe that Eq. (7) descends from a general property of any space where a normal chain displacement length distribution takes place. So, as Gaussian statistics of subchains is typical for real dry polymer networks (i.e., without solvent$^{(19)}$), when $\bar{L} = l < \infty$ Eq. (7) evaluates the displacement from the pure normal case.

In (ii), Eq. (8) is a decreasing function of y, and we have:

$$\lim_{\bar{L} \to l} b(y) = \begin{cases} 1 & l = \infty \\ 0 & l = 0 \end{cases} \tag{10}$$

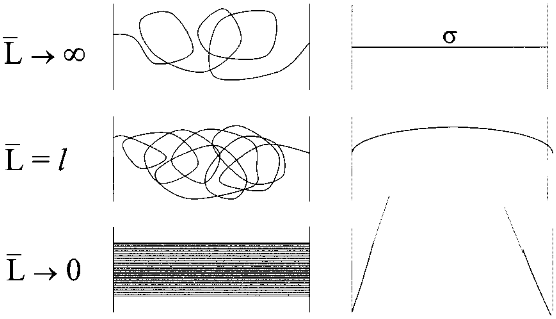

Fig. 2. Sketch of the geodesic length increase with decreasing BL constant.

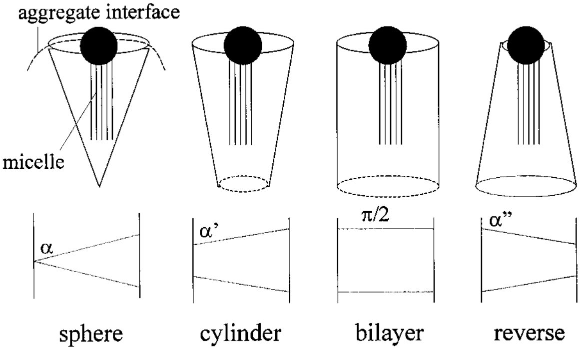

Fig. 3. Sketch of the available volume per micelle interpreted as the space contraction (or dilatation) determined by a $\bar{L}$ variation (see Eq. (8)).

Here, the average dimension $\bar{\varrho}$ converges to $\mathscr{L}$ when the space is Euclidean, while decreasing the BL constant gives a space contraction. From its definition, the quantity b is expected to be increasing with the increase of the so-called dimensionless packing parameter, which estimates the volume per chain length.$^{(20)}$ It reads $p \sim v/s_0 l_c$, v being the volume per micelle, s_0 the optimal area per headgroup and l_c the maximum length that the tail can take. Typical values go from $p \sim \lesssim \frac{1}{3}$ for spherical aggregates, to ~ 1 for planar bilayers, while $p > 1$ denotes inverted structure formations.$^{(21)}$ Correspondingly, the geometrical shape varies from conic to cylindric, and changes orientation when the system is inverted, from cylindric to conic. Thus, a relationship between Eq. (8) and micellar shape can be set. Figures 3–4 reports qualitatively the packing parameter interpreted as the space contraction/dilatation directly pointed out by Eq. 8) (say, as it would be $p \sim b^3$, with $v = 1$). Correctly, if the volume available is a cylinder (planar structure), the parallelism angle turns out to be $\pi/2$. It decreases

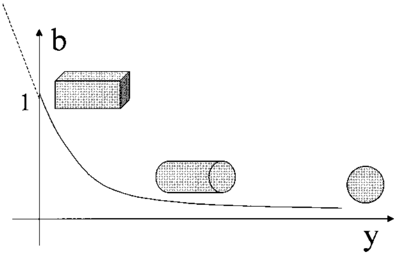

Fig. 4. Graphical illustration of the correspondence between shape of micellar aggregates and Eq. (8).

towards lower values when spherical aggregates form, and increases up to π in inverted systems.[(22)]

To work out Eqs. (7)–(8), we have to relate physics to space curvature through the BL length, keeping in mind that $1/\bar{L}$ should increase with molecular weight (M), concentration (c) and/or other quantities associated.[(5)] The approximations maken, like $L \to \bar{L}$ and rather simple distribution functions, do not suit the description of complex geometrical transitions, particularly in the second case (ii). On this basis, in the following we restrict ourselves to deal with swelling of polymer networks[(23)] and simple growth phenomena of micellar aggregates.[(24)] We will see that the agreement between theory and experiments is quite satisfactory in all cases examined.

In Figs. 5a–b the equilibrium volume swelling parameter, α, has been plotted against M^*, where $M^* \in [0, 1]$ is a reduced molecular weight,

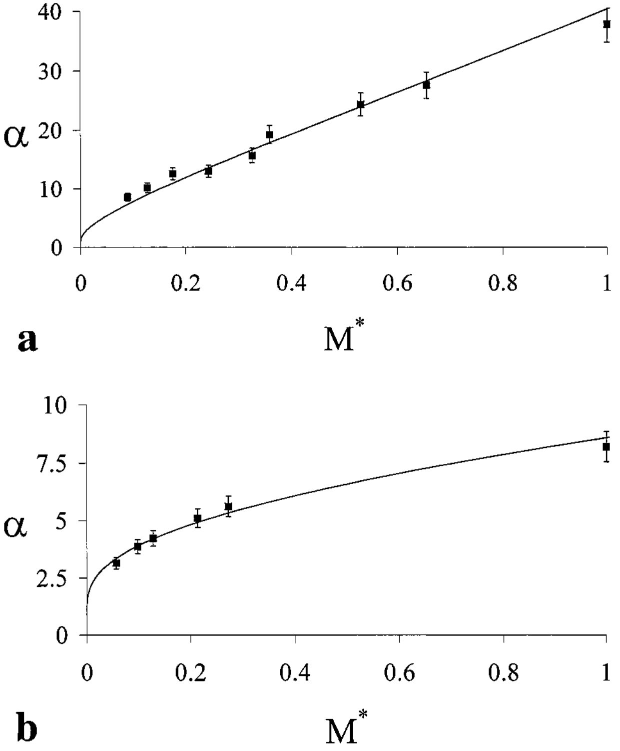

Fig. 5. Experimental swelling degree behaviour versus reduced molecular weight, α vs M^*, in the systems (a) polystyrene-benzene and (b) poly (dimethylsiloxane)-toluene. Solid lines denote theoretical curves of the form $a^3 = a^3(x)$, where $x \propto M^{*\chi}$ and $\chi > 0$.

normalized to the maximum extrapolated value. Systems under consideration are (5a) polystyrene-benzene and (5b) poly (dimethylsiloxane)-toluene, both at about the room temparature. All details can be exhaustively found elsewhere.(25) Expressing α as a function of a, simply requires to remind the definition of swelling degree, i.e., $\alpha = V/V_0 \sim a^3 > 1$, where V_0 and V stand respectively for network volumes in dry and isotropically swollen states. In (5a) the scaling law of the end-to-end distance is shown when excluded volume effects are considered in a good solvent, $\alpha \sim M^{3/5}$. Figure 5b shows instead $\alpha \sim M^{3/8}$. To get a description of both locus points, we can build a best fit function on Eq. (7) and the phenomenological dependence $x = mM^{*\chi}$ ($\propto 1/\bar{L}$), $m > 0$ and χ beings heuristic coefficients. As $\bar{L}$ should decrease with increasing M we expected $\chi > 0$ and, in the end, the sets of values $m \simeq 0.67$; $\chi \simeq 0.10$ (5a), $m \simeq 0.54$; $\chi \simeq 0.07$ (5b) are found.

Figure 6 refers to the experimental work presented in ref. 26. It indicates the behaviour of the apparent hydrodynamic radius of micelles (R_m) in aqueous solutions of sodium do decyl-dioxyethylene-sulfate, at the room temperature and with a counterionic strenght equating $[\mathrm{Al}^{3+}] \simeq 2.4$ mM. Specifically, the dependence of the reduced radius $R^* \in [0, 1]$ is here plotted against the inverse of a reduced counterion concentration, $c^* \in [0, 1]$. It has been established that this system undergoes a sphere-to-rod transition which is sensible to the net charge of dissolved multivalent counterions. Increasing the concentration of the ion Al^{3+}, which is able to bind together three surfactant headgroups at the micelle interface, decreases the mean area per headgroup and therefore increases the packing parameter.(21) If so, we can set $y = m/c^{*\chi}$, still with $\chi > 0$, and the best fit function based on Eq. (8) with(24) $v = 2$ now returns $m \simeq 3.95$; $\chi \simeq 0.81$.

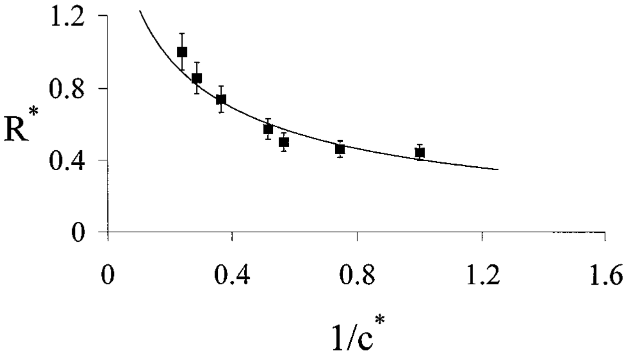

Fig. 6. Experimental behaviour of the reduced hydrodynamic radius of micelles against the inverse of the reduced counterion concentration, R^* vs $1/c^*$, in aqueous solutions of sodium dodecyl-dioxyethylene-sulfate. Solid lines denote theoretical curves of the form $b = b(y)$, where $y \propto c^{*-\chi}$ and $\chi > 0$.

CONCLUSIONS

1. The Bolyai–Lobachevskij (BL) formula has been employed to write a curvature-dependent partition function defined over a Non-Euclidean space.

2. Introducing a principle of equivalence like Boltmann factor ↔ BL length, brings us to a relation for the average geodesic path as a function of curvature. It is the analogy to the basic equation for average energy and partition function, in the energy representation, and provides a simple geometrical interpretation of statistical thermodynamics.

3. A polymer chain in solution has been recently tackled as a perturbation to the Minkowskian metric of a relativistic space, structured by a covariant diffusion law. The equation achieved (see Eq. 6) is thus expected to be suitable for describing geometrical properties of polymer networks.

4. Use of simple distribution functions (i.e., Gaussian and exponential) and mean BL lengths, allowed us to interpret simple experimental data of swelling and micellar growth. In the second case, a variation in the so-called packing parameter can be seen as a length contraction-dilatation of the space hosting the micelles.

APPENDIX

(i) Polymer Chain. Consider the partition function defined in Eq. (5) as:

$$Z_\lambda = \int_0^\infty e^{-r/\bar{L}} \zeta(r)\, dr \tag{11}$$

If one adopts$^{(4, 17)}$ $\zeta(r) \propto e^{-r^2/\pi\sigma^2}$, then gets:

$$Z_\lambda \propto \sqrt{\frac{\pi}{2}}\,\sigma e^{\sigma^2/\pi\bar{L}^2} \left\{1 - \Phi\left(\frac{\sigma}{\pi^{1/2}\bar{L}}\right)\right\} \tag{12}$$

Φ denoting the so-called probability (or error) integral:$^{(27)}$

$$\Phi(z) = \frac{2}{\pi^{1/2}} \int_0^z e^{-t^2}\, dt \tag{13}$$

In accordance to Eq. (12):

$$d \ln Z_\lambda = d \ln \sigma + \frac{1}{\pi} d\left(\frac{\sigma^2}{\overline{L^2}}\right) + d \ln \left\{1 - \Phi\left(\frac{\sigma}{\pi^{1/2}\bar{L}}\right)\right\} \tag{14}$$

and, from the root mean square constancy, Eq. (6) becomes:

$$\bar{\varrho}(\sigma, \bar{L}) = \frac{\sigma e^{-\pi\sigma^2/4\bar{L}^2}}{1 - \Phi(\pi^{1/2}\sigma/2\bar{L})} - \frac{\pi\sigma}{2\bar{L}} \tag{15}$$

Eq. (15) coincides with Eq. (7), once the new variables $a = \varrho/\sigma$ and $x = \pi^{1/2}\sigma/2\bar{L}$ are set.

(ii) Micellar chain. In this case,$^{(17, 18)}$ if $\zeta(r) \propto e^{-r/\mathscr{L}}$, one obtains at once (see Eqs. (5)–(6)):

$$Z_\lambda \propto \frac{\bar{L}\mathscr{L}}{\bar{L} + \mathscr{L}} = \bar{\varrho} \tag{16}$$

which is just Eq. (8), provided $b = \bar{\varrho}/\mathscr{L}$ and $y = \mathscr{L}/\bar{L}$.

More generally, let $\zeta(r) \propto r^{\nu-1}e^{-r/\mathscr{L}}$ and $\nu \in \Re^+$, we yield:

$$Z_\lambda \propto \left(\frac{1}{\bar{L}} + \frac{1}{\mathscr{L}}\right)^{-\nu} \Gamma(\nu) \tag{17}$$

Since the Gamma function $\Gamma(\nu)$ (Euler integral of the second kind) does not depend upon λ, we have in the end the same Eq. (8) for the rescaled quantity $b = \bar{\varrho}/\nu\mathscr{L}$.

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11. In the following, we will call L as the Bolyai–Lobachevskij (BL) characteristic length, or constant. Formally speaking, it should be observed that $1/L$ must not be confused with the so-called Gaussian ($\sim 1/\varrho^2$) and average ($\sim 1/\varrho$) curvatures. See, for instance, M. P. Do Carmo, *Differential Geometry of Curves and Surfaces* (Prentice–Hall, Englewood Cliffs, New Jersey, 1976).
12. Note that the quantity $e^{1/L}$ is equal to the constant ratio between the arc lengths of two coaxial horocycles, bounded by the same radii and distant by the unit length. In hyperbolyc geometry, a horicycle denotes a circle with infinite radius and corresponds to the straight line concept in the ordinary space. Precisely, consider a line l, point Q on l, and trace the perpendicular $\overline{PQ}$ through l to Q. Then, consider the circle δ, with center P and radius $\overline{PQ}$, which is tangent to l at Q. Recede then P from l along the perpendicular. The circle δ will increase in size, remaining tangent to l, and approaching a limiting position as P recedes arbitrarily far from Q. In Euclidean geometry, the limiting position of δ would just be the line l, but in a Non-Euclidean (or hyperbolic) space it is a new curve h, generally termed limiting curve or horocycle. See, for instance, E. B. Vinberg, *Geometry II —Space of Constant Curvature* (Springer-Verlag, Berlin, 1988).
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15. This position can be seen as a sort of mean field approximation.
16. Infact, let Z_ε be the ordinary partition function, we have:

$$Z_\varepsilon = \int \frac{\partial N_\varepsilon}{\partial \varepsilon}\, e^{-\beta\varepsilon}\, d\varepsilon = \int \frac{\partial N_\varrho}{\partial \varrho}\, e^{-\varrho/L}\, d\varrho$$

because of Eq. (5) and $(\partial N_\varepsilon/\partial\varepsilon)\, d\varepsilon \equiv \zeta(\varrho)\, d\varrho$, with $\zeta(\varrho) = (\partial N_\varrho/\partial\varrho)$.
17. Note that, from the definition of partition function, the Gaussian distribution can be equivalently rewritten unless of a proportionality constant, not important here. We have only to require that (i) $\bar{\varrho} = \sigma$ and (ii) $\bar{\varrho} = \mathscr{L}$, when $\bar{L} \to \infty$.
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