

Current opinion: What is a nanoplastic?[☆]

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ABSTRACT

With the large amount of attention being given to microplastics in the environment, several researchers have begun to consider the fragmentation of plastics down to lower scales (*i.e.*, the sub-micrometer scale). The term “nanoplastics” is still under debate, and different studies have set the upper size limit at either 1000 nm or 100 nm. The aim of the present work is to propose a definition of nanoplastics, based on our recently published and unpublished research definition of nanoplastics. We define nanoplastics as particles unintentionally produced (*i.e.* from the degradation and the manufacturing of the plastic objects) and presenting a colloidal behavior, within the size range from 1 to 1000 nm.

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1. Introduction

With the large amount of attention being paid to microplastics released in the environment, several researchers have begun to consider the fragmentation of plastics down to a very small scale, below 1 μm (Andrady, 2011; Cózar et al., 2014; Ter Halle et al., 2016). The term nanoplastics is still under debate, and some authors set the upper size limit at 1000 nm while others at 100 nm (Cole et al., 2015; Cole and Galloway, 2015; Crawford and Quinn, 2017; da Costa et al., 2016; Koelmans et al., 2015; Ter Halle et al., 2017). This latter value is related to the current definition of manufactured nanomaterials that have received much attention over the last decades but it remains inappropriate from the point of view of colloidal physics and chemistry. Based on this loose definition, several eco-toxicological researches have used engineered plastic

nanomaterials, in particular, polystyrene latex nanomaterials (PSL), and reported potential effects (Bergami et al., 2017; Chen et al., 2017; Nolte et al., 2017; Rist et al., 2017). However, the use of PSL as a model for plastic could lead to biased measurements and unrepresentative results (Phuong et al., 2016). To the best of our knowledge, no current definition is available in the literature defending and explaining the relevancy of the word “nanoplastics”. On the basis of recent studies, our past works and current projects concerning nanoplastics in the environment, we propose the following definition: nanoplastics are particles within a size ranging from 1 to 1000 nm resulting from the degradation of industrial plastic objects and can exhibit a colloidal behavior.

2. Where do nanoplastics come from?

A plastic is a formulated polymer to which additives have been added to give physical properties required for commercial purposes (color, mechanical properties, resistance to solar irradiation, to bacterial or fungal attacks ...). Plastic debris is an abandoned plastic

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object in the environment. This debris can break down into different size fractions. Microplastics has been the most studied size category of plastic debris for several decades (Andrady, 2011; Wright et al., 2013). Nevertheless, no universal definition exists. For microplastic, we may adopt here the definition lately given by Galgani et al. (2013) that has been recently proposed for the European Water Framework Directive: namely a microplastic corresponds to the size range 1–5 mm and small microplastic to the range 25 μm to 1 mm. It is to be noted that the term “micro” is used for objects of millimetric size and may also be associated with the Ancient Greek meaning of “μικρός: small” and not with the meaning of the metric scale prefix. In that sense, the 1–25 μm materials may be considered microplastics to some. The lower size limit of microplastics was fixed by the mesh size cutoff of the *manta* trawl nets used to sample microplastics in the environment (Andrady, 2011). In our opinion, nanoplastic results from the degradation of plastic objects and could be formed during the break-down of aged-microplastics, the manufacturing process, or even during the use of the object (Bouwmeester et al., 2015).

3. Why use “nano” for plastics?

One of the largest criticisms of researchers using the prefix “nano” concerns the fact that it may be just a trick to get the attention of the public, politicians and funding agencies. The last twenty years have shown increasing awareness of the environmental risks of manufactured nanomaterials, and numbers of projects have been funded internationally on this issue even though resources to examine the environmental implication of nanomaterials are stalling. In our approach, the prefix “nano” in nanoplastics is used to match with the terms macroplastics and microplastics. We propose the term nanoplastics to define the size of the plastic litter, such as a single particle or in homo- and/or heteroaggregates form, and refers to any plastic from 1 nm to 1 μm in size. For nanoplastics, we do not define the plastic size according to limitations in the sampling technique or the visualization and characterization of the analytes but to their real and physical size.

4. Nanoplastics are different from manufactured nanomaterials

There are no analogies possible between nanoplastics and others “nanomaterials” due to the different production pathways and physical and chemical properties. According to the International Standard Organization, a manufactured nanomaterial is “intentionally produced for commercial purposes to have specific properties or specific composition” (ISO/TS 80004–1:2015). The specific physical and chemical properties are generally the size, shape, surface, composition, (Brar et al., 2010; Colvin, 2003; Ju-Nam and Lead, 2008; Weinberg et al., 2011) and cannot be extrapolated to nanoplastics. In the Nano-Environmental Health and Safety programs, a large number of researchers has considered manufactured nanomaterials and their possible release and impact on the environment.

On the other side, nanoplastics result from the erosion or breaking down of larger plastic debris and, contrary to manufactured nanomaterials, there are no reasons for the selection of a size. Nanoplastics are consequently highly polydisperse in physical properties and heterogeneous in composition (Gigault et al., 2016; Lambert and Wagner, 2016; Ter Halle et al., 2017). Indeed, because nanoplastics are produced unintentionally from the degradation of microscale plastic litter, it is highly probable that nanoplastics form heteroaggregates with other natural and/or anthropogenic materials (Hüffer et al., 2017). In environmental systems, colloids are usually heteroaggregates including clays and organic materials

(Hotze et al., 2010). Consequently, their surface and structure are generally uncontrolled and conditioned by the physical and chemical parameters of the system (pH, salinity, natural organic matter ...). Additionally, through different mechanisms, different surface speciation can be found on a single heteroaggregate (Hotze et al., 2010).

5. The colloidal behavior of nanoplastics is relevant

Some plastics, such as poly(vinyl chloride) (PVC - density 1.4 g/cm³), are dense enough to settle in water at the macroscopic level. Nevertheless, based on our on-going work at the nanoscale, we found PVC particles dispersed in the sea water column (Ter Halle et al., 2017). The presence of PVC at the nanoscale may be explained by the size change of the particle from the macroscale to the nanoscale. At the macroscale, the particles dispersion in water are mainly governed by the buoyancy/sedimentation properties, directly correlated to their density and shape (film vs sphere). When the particles reach the micro-scale they can interact with micro-organisms (bacteria, phytoplankton) which could modify their buoyancy either in a positive and negative manner (Lagarde et al., 2016; Long et al., 2015). When the particle size reaches the nanoscale, collisions with water molecules and other present ionic species may prevent the particle from sedimentation. The resulting effect of this interaction is random motion throughout the solution, called Brownian motion. At particle sizes of few micrometers, Brownian motion becomes appreciable while it is predominant at size approaching 100 nm (Hassan et al., 2015).

A rapid experiment to define plastic debris involves determining the size limit at which the plastic species begin to display macroscopic behavior (buoyancy and/or sedimentation rate). This limit is dependent on the plastic composition and the dispersion media (including the biota), and further investigations are needed. Any particle having a linear dimension between 10^{−9} m (1 nm) and 10^{−6} m (1 μm) is considered as a colloid (IUPAC, n.d.) and may be found in solution either under isolated or aggregated form, depending on their environment (pH, ionic strength, temperature, dissolved organic matter etc.), which needs to be jointly characterized.

The ionic strength of the dispersion medium (generally fixed with a monovalent salt such as sodium chloride) directly influences the Debye length, and therefore the particle-particle electrostatic repulsion. An increase of the ionic strength leads to a decrease of the Debye length and a decrease of the electrostatic interaction. The ionic strength at which the aggregation starts is called the critical coagulation concentration (CCC) and is a characteristic of a given colloidal system (Holthoff et al., 1996).

As illustrated in Fig. 1, the aggregation of nanoplastics depends on the ionic strength. In a preliminary study (Fig. 1a), we demonstrated that environmentally relevant polystyrene (PS) nanoplastics are stable in an aqueous solution containing 350 mmol L^{−1} of NaCl, while they start to irreversibly aggregate above 500 mmol L^{−1} of NaCl. Like all other colloidal species, nanoplastics present both these stability behaviors. The size, shape, and concentration of the aggregates determine the properties of the nanoplastic dispersion. Indeed, nanoplastics may directly associate with dissolved organic and inorganic colloids to form both stable and unstable aggregates in the given physical (UV light, temperature, etc.) and chemical (ionic strength, pH, etc.) conditions of the dispersion medium.

6. Polymer latex standards are not a model for nanoplastics

Fig. 2 shows electronic microscopy images of nanoplastics of polyethylene degraded by UV from microplastics sampled in North Atlantic (Fig. 2a) and a mixture of PSL standards (Fig. 2b). Nanoplastics show open structures (Fig. 2a), which are highly similar to

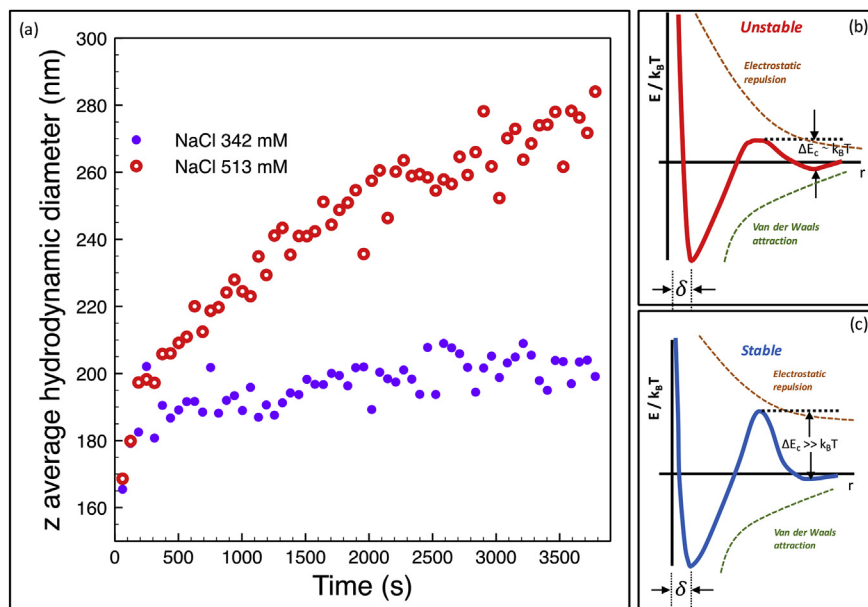


Fig. 1. (a) Our data show the evolution of the z-average hydrodynamic diameter of nano-PS at two NaCl concentrations according to the time. The nano-PS was purchased from Cordouan Technologies and synthesized to be similar to the ones naturally obtained weathering of large scale polystyrene. (b–c) Schematic illustration of the kinetic stability show the interaction energy E as a function of the separation distance r of two particles (k_B and T are the Boltzmann constant and the temperature, respectively). As two particles approach in a colloidal dispersion, the energy barrier ΔE_c can be (b) on the same order of magnitude as the thermal energy $k_B T$, leading to an unstable dispersion, or (c) $\Delta E_c \gg k_B T$, leading to a stable dispersion.

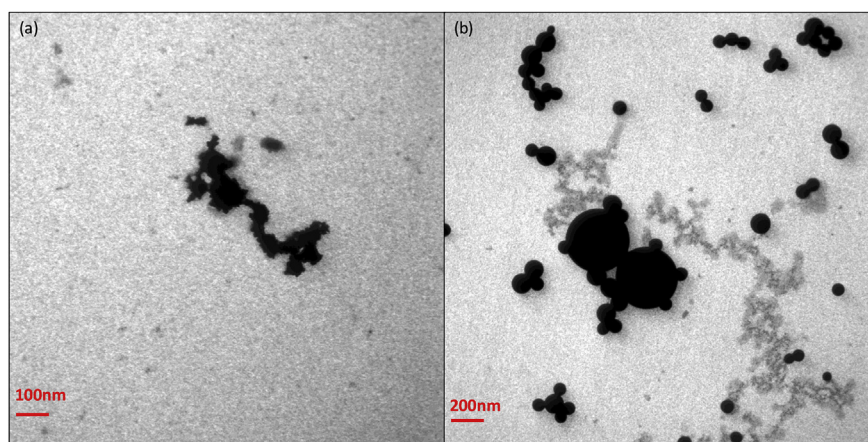


Fig. 2. Transmission electronic microscopy of (a) environmentally relevant nanoplastics of polyethylene degraded by UV from aged-microplastics sampled in the North Atlantic Ocean; (b) a mixture polystyrene standards latex (80, 100, 200 and 400 nm, purchased from Thermo-Fischer scientific). The gray forms are characteristics of organic molecules (surfactants) generally used to stabilize polystyrene standards latex.

the fractal nature of aggregates and no single parameter can be used to describe the particle population (Gigault et al., 2016). For PSL, the size and shape are perfectly defined and controlled, as well as their surface composition (anionic, cationic, fluorescence, ligand stabilized). A uniform shape (mostly spherical) is generally considered for calibrating instruments or determining properties (for instance, the optical properties of rod- and star-shaped gold nanomaterials). Spherical particles can be characterized by a single parameter that is constant within the population distribution, i.e., the radius.

7. Current issues about nanoplastic

Our definition of a nanoplastic is a particle coming from the fragmentation of a macro- and/or microplastic. Table 1 summarizes

the main physical and chemical parameters defining a nanoplastic. Nanoplastics present colloidal properties in aqueous system with sizes ranging from 1 nm up to 1000 nm and result from the degradation of industrial plastic objects. This definition excludes the use of the term nanoplastics for any manufactured nanomaterials present in our common products (cosmetics, materials, biomedical).

We recently demonstrated in the analysis of sample from North Atlantic Ocean that the colloidal solution containing nanoplastics are generally composed of several plastics. According to their formation and transformation pathways, it is highly probable that nanoplastics are heteroaggregates of plastic particles with other natural species (organic matter, trace metal, metal oxides).

The formation of nanoplastics under laboratory conditions from plastic objects has been demonstrated (Lambert and Wagner, 2016)

Table 1

The main properties that define nanoplastics.

Composition	Mixture of various polymers, highly weathered
Formation	Unintentional
Size	1 nm – 1 µm
Size distribution	Polydisperse (continuum of size)
Shape	Asymmetrical shape; Heterogeneous
Surface charge	Uncontrolled with the presence of different species (organic and inorganic); Inhomogeneous on the particle surface
Stability	Heteroaggregation with other natural and/or anthropogenic colloids during the formation process;
	Depending of both nanoplastics and its surrounding media physical and chemical properties
Aggregates	Potentially, fractal aggregates form;
	Depending on the formation process
Porosity	Open structure;
	Depending on both the core material and the formation process

together with their formation from microplastic collected at sea (Gigault et al., 2016). Recent work has also identified nanoplastic in real seawater sampled from the North Atlantic subtropical gyre (Ter Halle et al., 2017). The scientific community still has to make a major effort to develop methods for the identification and especially quantification of nanoplastics in natural samples. The full characterization of these nanoplastics is a challenge as many questions are addressed like: what is the state of weathering of the polymer in nanoplastics? Are nanoplastics still associated with additives? Are they associated with organic pollutants? Or heavy metals? It is necessary to develop analytical methods adapted to characterize the physical properties and the chemical composition of these nanoplastics and to study the evolutions with respect to aging of plastic debris within the continuum of size categories (from macroscopic, to micrometric down to the nanoscale).

Compared to macro- and microplastics, it is even more inconceivable to develop a removal strategy for nanoplastics. Due to their size and high diffusion properties, it is not possible to consider this option, which bring new questions in the context of the “Planetary Boundaries” (Jahnke et al., 2017). One option would be to include nanoplastics within the planetary boundary of chemical pollution. But according to the implication of nanoplastics in all our life and the plastic litter situation, we argue that a new, specific planetary boundary for plastic litter should be established.

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