

# Direct observation of polymer gel surfaces by atomic force microscopy

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We report here, for the first time, the direct observation of the submicron structure of gel surfaces in water by using an atomic force microscope (AFM). We present also its change in response to external stimuli; we investigated, among the variables that affect the topography of the gel surface, the effect of the network density of poly(acrylamide) gels and the effect of the temperature change of poly *N*-isopropylacrylamide gels. Gels were prepared with disklike shape of thickness ranging from 10 to 50  $\mu\text{m}$ , and one of the gel surfaces was chemically adhered onto a glass plate. Spongelike domains of submicrometer scale were found here on the gel surfaces, which was strongly affected by the cross-linking density (nature of the gel network) as well as the osmotic pressure (environmental condition), and also thickness (condition of constraint). The qualitative properties of the surface microscopic structure of gels are discussed in relation to a hypothetical model of two-dimensional gels based on the Flory–Huggins theory. These results disclose that the surface microstructures of polymer gels in solvent as well as the nanometer scale structural changes are associated with the gel phase transition. Moreover, they indicate that the potential for a new technology to control the domain size of the gel surface as well as its function by external stimuli could emerge, which would find a variety of applications in many fields, such as engineering, medicine, and biology. © 1996 American Institute of Physics. [S0021-9606(96)50704-0]

## I. INTRODUCTION

Gels of cross-linked polymer networks in liquid can undergo discontinuous volume phase transition in response to infinitesimal changes in any of several environmental conditions,<sup>1</sup> such as temperature,<sup>2</sup> light,<sup>3</sup> specific molecules,<sup>4</sup> and uniaxial stress.<sup>5</sup> The phase transitions of various gels have been extensively studied<sup>6</sup> and the macroscopic volume change can be easily observed using a tiny gel of submillimeter diameter<sup>3,7</sup> by an optical microscope. Various kinds of patterns develop in the gel surface during the phase transition resulting from slight change in external conditions.<sup>8,9</sup> The patterns in swelling and shrinking processes differ in their appearance and physical mechanisms. The induction of swelling patterns is a result of mechanical instability,<sup>8</sup> while the variety of types of shrinking patterns is mainly due to the mechanical constraints that have been theoretically explained in terms of macroscopic phase separation.<sup>9</sup> Almost all the experimental and theoretical investigations of network surface conformation have been limited to the macroscopic conformation in the size range at the millimeter to submillimeter level, and neither the microscopic aspects of the gel surface nor its change with the respects of the external stimuli has yet been explored. In this paper, we present, for the first time, direct observation of polymer gel surface in a liquid with an atomic force microscope (AFM).<sup>10</sup> The success in imaging polymers in water by Drake *et al.*<sup>11</sup> of 1989 signaled the imaging of soft materials in liquid. Reproducible images were observed by Hansma *et al.* in 1992 by measuring DNA in *n*-propanol.<sup>12</sup> The method has been widely disseminated and has now become reliable in many fields except gel science.<sup>13</sup> This paper deals with how the AFM can provide insights into gel science.

Our interest was focused on the surface conformation of gels in the size range from micrometers to submicrometers and the response of the conformation to the external stimuli. We investigated, among the variables that affect the conformation of the gel surface, the effect of the network density of poly(acrylamide) (AAM) gels as well as the effect of the temperature change of poly *N*-isopropylacrylamide (NIPA) gel. We present herein a theoretical simulation using a numerical model of a two-dimensional gel<sup>14</sup> based on the Flory–Huggins theory,<sup>15</sup> where the fluctuation of the cross-linking density in the pre-gel solution is assumed to be memorized in the gel at preparation and the local minima is sought by using the molecular dynamics method.<sup>14</sup> Here, a domainlike structure was obtained in a specific environmental condition. The microscopic surface structure of gels as well as the factors which determine the structure are discussed in qualitative terms with references to the theoretical model.<sup>14</sup> We attempt to demonstrate a general framework for developing gel technology using the gel surface and its change during the volume phase transition.

## II. GEL SYNTHESIS AND MEASUREMENT

Gels were synthesized by a free radical copolymerization reaction<sup>2,7</sup> between two glass plates with a spacer of thickness ranging from 10 to 50  $\mu\text{m}$ . In this synthesis, one of the gel surfaces is chemically adhered onto a glass plate. Bind Silane (Pharmacia) was rinsed on one glass plate before dipping it into the pregel solution to adhere the gel chemically onto it. For the standard AAM gels (designated as 1BIS-AAM) synthesis, a mixture of 5 g of AAM (Wako) and 133 mg of *N,N'*-methylene-bis-acrylamide (BIS, cross-linker, Wako) was dissolved in 100 g water. After the solu-

tion was fully saturated with nitrogen, 40 mg of ammonium persulfate (APS, initiator, Wako) was added to it. The gelation was carried out for 1 h at 60 °C. The standard NIPA gels (designated as 1BIS-NIPA) were prepared from a mixture of 7.8 g of NIPA (Kodak), 133 mg of BIS, and 240  $\mu\text{l}$  of *N,N,N',N'*-tetramethylethylenediamine (accelerator, Wako) dissolved in 100 g water. After bubbling with nitrogen, 40 mg of APS was added, initiating the gelation, which was carried out overnight at 0 °C. The number of monomers as the main constituent was fixed, and only the cross-linking density was changed. After gelation, one glass plate was removed from the gel, thus forming a clamped disk gel on the other glass plate. The gel was then immersed in a large amount of deionized, distilled water to wash away residual chemicals and unreacted monomers from the polymer networks.

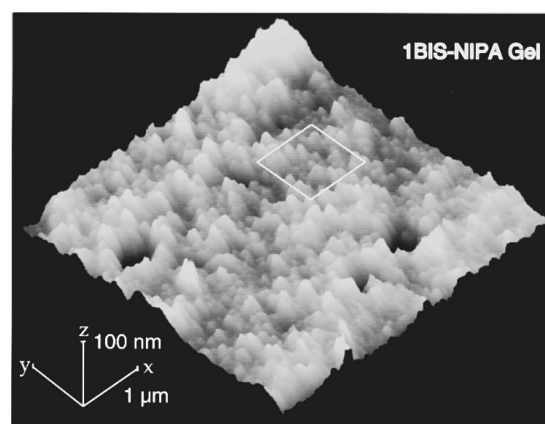
The microscopic image of the gel surface was determined using an AFM (Digital Instruments, NanoScope III) with Nanoprobe of 200  $\mu\text{m}$  length, a pyramidal oxide-sharpened silicon nitride cantilever. The constant force mode was utilized at the lowest possible set point voltage in order not to risk unnecessary damage to the gel. The images were processed only by flattening to remove background slope. Gel on a glass plate was placed in a specially designed temperature-controllable sample cell with water, and the temperature was regulated within  $\pm 0.05$  °C.

### III. RESULTS AND DISCUSSION

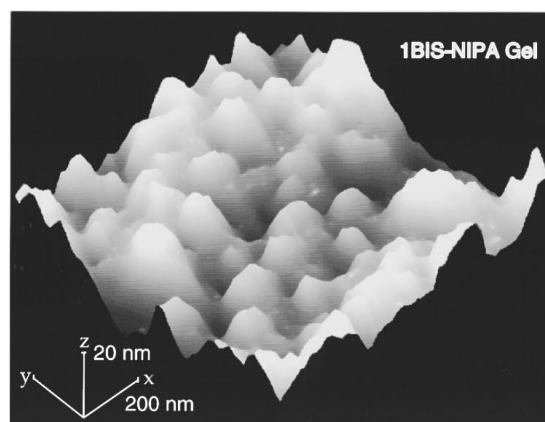
#### A. AFM observation

An equilibrium surface image of 1BIS-NIPA gel at 25 °C is shown in Fig. 1. In the image with scan size of  $5\ \mu\text{m} \times 5\ \mu\text{m}$  [Fig. 1(a)], there are undulations on the order of a few micrometers, large holes, and projections, among which there are flat regions with area of submicrometer size. An example of such a flat region was zoomed in as shown in the microimage with  $1\ \mu\text{m} \times 1\ \mu\text{m}$  scale [Fig. 1(b)]. A similar image of 1BIS-AAm gel at 25 °C is shown in Fig. 2(a). By inspecting these figures, one can observe spongelike domains, typically of 100 nm size in NIPA gel and of 10 nm size in AA m gel. The domain size was found to depend on the monomer property such as hydrophilicity or hydrophobicity as well as the environmental conditions at preparation such as the temperature. The gel in solvent developed a spongelike pattern of submicrometer scale on the surface, which did not appear similar to the submillimeter pattern observed in the extensive swelling kinetics of gel.<sup>8</sup> It should be noted that the appearance of the pattern due to Repel Silane was not so pronounced that it disturbed the present observations.

The effect of the cross-linking density was examined by measuring the surface images of the 4BIS-AA m gel with fourfold greater cross-linking density than the standard 1BIS-AA m gel under the same conditions [Fig. 2(b)]. The overall images for this gel were appreciably different from those for the 1BIS-AA m gel; the amplitude as well as the total domain number of 1BIS-AA m gel were much larger than those of 4BIS-AA m gel. To characterize the surface



(a)



(b)

FIG. 1. AFM microimage of NIPA gel surface in water at 25 °C (image size of  $5\ \mu\text{m} \times 5\ \mu\text{m}$ ) (a), and the flat square area denoted by the white solid lines was zoomed in (image size of  $1\ \mu\text{m} \times 1\ \mu\text{m}$ ) (b). The vertical scale has been greatly exaggerated to display the spatial amplitude in the  $z$ -direction clearly. Spongelike domains are visible in submicron scale.

roughness, we obtained the root-mean-square's for the same data of 1BIS- and 4BIS-AA m gels to be 1.2 and 0.73 nm, respectively. One could expect that when the cross-linking density is increased, the domain structure would be reduced. Moreover, for the interpretation of the surface conformation, it is useful to analyze the power spectrum, that is the magnitude squared of the Fourier transform of the amplitudes. The log-log plots of the power spectral density vs frequency of each system exhibited the linear relation for a wide range. We obtained the surface fractal dimension,<sup>16</sup>  $D = (7 - \text{slope})/2$  to be  $2.4 \pm 0.05$  and  $2.3 \pm 0.05$  for 1BIS- and 4BIS-AA m gels, respectively. The decrease of  $D$  by the increase of the cross-linking density corresponds to the decrease of the roughness. It is desirable to measure the images in various scales to confirm whether the gel surface is the self-similar fractal structure.<sup>17</sup>

Another experiment was performed to demonstrate the effect of temperature change as an external stimulus using 3BIS-NIPA gel with threefold greater cross-linking density than the standard 1BIS-NIPA gel. Comparison of the image

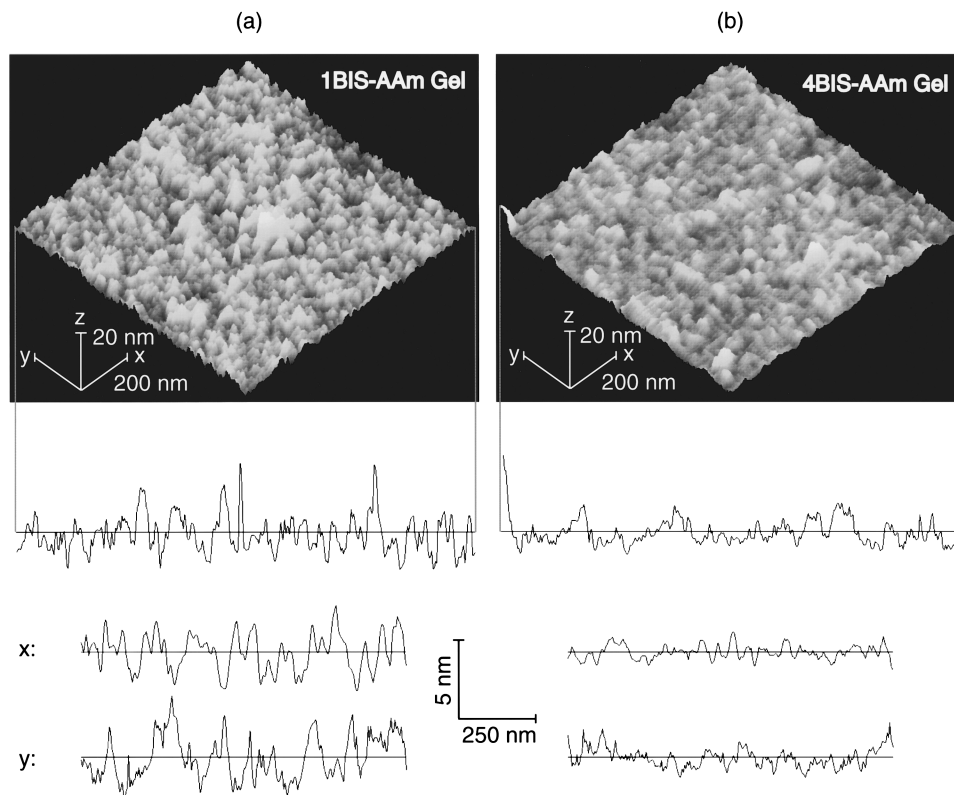


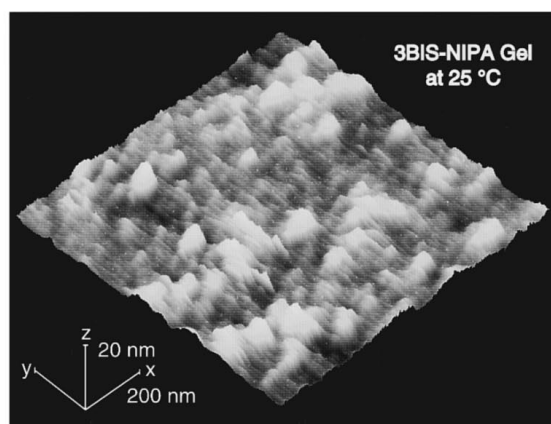
FIG. 2. Effect of the cross-linking density: AFM microimage of 1BIS-AAm gel surface (a) and 4BIS-AAm gel surface (b) in water at 25 °C (image size: 1  $\mu\text{m} \times 1 \mu\text{m}$ ). When cross-linking density was increased, the amplitude due to spongelike domains are less clear. Each bottom inserts are cross-sectional plots of the AFM images along the indicated diagonal,  $x$ , and  $y$  directions in this order.

of the 3BIS-NIPA gel [Fig. 3(a)] with that of the 1BIS-NIPA gel revealed that the domain structure of the former was reduced because of the increase of the cross-linking density, a result that is consistent with that in the AAm gels. When the temperature was kept at 25 °C, the gel would have been the swollen state with a volume change upon increase of the temperature. In spite of the mechanical constraint,<sup>5</sup> it would have entered the collapsed phase at 38 °C, since this temperature is much higher than the transition point of the unconstrained gel (33.6 °C). At 38 °C, the spongelike domain was evident [Fig. 3(b)]. It could be expected that when the gel takes the collapsed state by the attractive force (hydrophobic interaction), the domain structure would be enhanced.

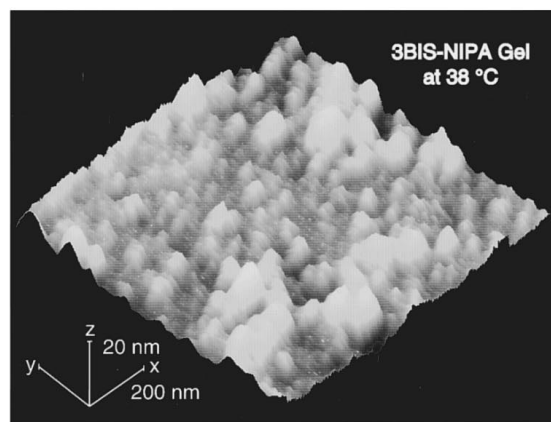
There are several possibilities in the interpretation of the relationship between the domains in the AFM topography and the polymer structure. The most fundamental explanation rests on the structural inhomogeneities in gels.<sup>18</sup> When the volume change is macroscopic (in the size range from millimeters to submillimeters), the observed volume should be reflected by the average network structure, while in the case of volume change in the size range from micrometers to submicrometers, the structure of the gel networks should have an important role. First of all, the permanent structural inhomogeneities must be taken into account, because a true network of gels should not be much different from an ideal network that is topologically similar to an ideal crystal lattice, but includes the network defects.<sup>19</sup> With the free radical

copolymerization, the fluctuation of the pre-gel solution where the monomers are under thermal fluctuation would be frozen into the network structure of gels.<sup>18,20</sup> As a result, the final network of gels should have the distribution of polymer concentration as well as cross-linking density which is permanently memorized in the gel. Second, even if the distribution of cross-linking in a network is uniform at preparation, it can become less uniform and inhomogeneous upon swelling.<sup>21</sup> In this swelling inhomogeneity, a gel undergoes temporal thermal concentration fluctuations.<sup>18</sup> The random cross-linking density generates long-lived fluctuation of structure such as local topological imperfection<sup>21</sup> in the swollen networks which can destroy the uniform cross links. The high-energy barriers may trap the system in the domain structures. These fluctuations can account for the nature of the spongelike domains.

Another important factor for the surface domain structure is that related to the mechanical constraint in one of the surfaces. In fact, with increase of the gel thickness, the constraint condition in the other free surface of the gel should be progressively more loosely applied, and consequently the AFM images were found to become blurred. This is because the thermal dynamical fluctuation depends on the constraint. It seems important to investigate further the physical basis of the submicrometer pattern as well as the dynamic properties of the pattern formation as a function of the thickness. It can be concluded, however, that the domain structures do exist



(a)



(b)

FIG. 3. Effect of temperature change: AFM microimage of NIPA gel surface in water at 25 °C (a) and at 38 °C (b) (image size:  $1\ \mu\text{m} \times 1\ \mu\text{m}$ ). When temperature was increased, the amplitude due to the spongelike domains are more clear.

even when the constraint has been removed, since they were observed in 3BIS-NIPA gels at 25 °C whose volume is almost same as that at preparation, therefore mechanical constraint can be neglected. We believe that the domain structure is probably enhanced by the mechanical constraint.

## B. Computer simulation

There appeared two interesting features that should be noted in the observation of the surface structure of the gels: First, the originally rough surface of the AAm gels with low cross-linking density became smooth if the cross-linking density was increased, and second, when the temperature of NIPA gel was raised beyond the transition temperature, spongelike domain was evident. We shall attempt below to explain these features using the two dimensional model gel<sup>14</sup> based on the Flory–Huggins theory.<sup>15</sup> The free energy consists of two contributions of mixing free energy,  $f(\lambda_1\lambda_2)$  and the elastic energy,  $\nu_0(\lambda_1^2 + \lambda_2^2)/2$ , where  $\lambda_1$  and  $\lambda_2$  are the swelling ratio along each axis,  $\nu_0$  is the cross-linking density, and  $f(\lambda_1\lambda_2)$ , a function of the local swelling ratio,  $s = \lambda_1\lambda_2$ , can give the swelling pressure,  $\omega(s) = -df(s)/ds - \nu_0$  that

was assumed to be  $-(s-s_1)(s-s_2)(s-s_3)$  with  $0 \leq s_1 \leq s_2 \leq s_3$ . The model gel can take the collapsed and the swollen states at  $s = s_1$  and  $s_3$ , respectively, and the total free energy is functions of the parameters  $(s_1, s_2, s_3, \nu_0)$ . In this model, the gel was assumed to consist of elementary triangles,  $\nu_0$  was assumed to be constant within the element, and the deformation was assumed to be uniform, thus making the continuum model into discrete one. With the computer-generated uniform random number,  $\nu_0$  was randomly given to each element. The initial condition was constructed as follows:  $\nu_0$  of an element was replaced by averaging four  $\nu_0$  values, that is,  $\nu_0$  of the target element and the  $\nu_0$  for its surrounding three elements. This averaging was repeated ten times. The equilibrium swollen state and the time evolution were obtained by the same method described in Ref. 14. We have calculated numerically for the system of  $50 \times 50 \times 2$  regular triangle elements on the assumptions of the periodic boundary condition as well as constant total area due to the mechanical constraint. The set of curves in Fig. 4(a) shows the free energy profiles without mechanical constraint where the mixing free energy term is dominant, since the elastic energy term changes monotonically as a function of volume as well as unsensitively as a function of temperature.<sup>22</sup> At most temperatures, there is only one minimum and hence only one possible volume corresponding to energy minimum. Between the variables of the swelling and shrinking transition, two local minima exist and the gel can take either swollen or collapsed state.<sup>23,24</sup> Now, we sought the local energy minima under mechanical constraint starting from the initial reference state,  $\lambda_1 = \lambda_2 = 1$  of a regular triangular lattice aforementioned. First, we calculated the volume phase separation between the swollen and collapsed phases. A spongelike domain between the swollen and the collapsed phases was obtained as shown by the distribution of vertex positions of triangle elements in Fig. 4(b), using the mixing free energy of a coexistent state. The profiles of  $f(s)$  and the distribution of the relaxed  $s$  value (density of states; DOS) are illustrated in the graph. Second, a similar calculation was conducted using the same mixing free energy of a swollen state at  $\nu_0 = 0.34$  [Fig. 5(a)] and at  $\nu_0 = 0.68$  [Fig. 5(b)]. From these figures, spongelike domain can be seen at  $\nu_0 = 0.34$  in spite of the swollen condition. The larger  $\nu_0$  can reduce the domain structure, and the surface became flat at  $\nu_0 = 0.68$ . This result indicates that the spongelike domain appears because for the gel with smaller  $\nu_0$  the total free energy of the domain structure is smaller than the single flat structure; the elastic energy gain which results from producing the domain structure is more than the mixing energy loss due to phase separation between the swollen and collapsed phases. The rough surface of the model gel with low  $\nu_0$  became smooth if  $\nu_0$  was increased two-fold. On the other hand, the relaxed configuration was obtained using the mixing free energy of a collapsed state, when  $\nu_0$  was fixed at 0.68 [Fig. 5(c)]. The spongelike domain was evident again when the gel networks were under negative osmotic pressure, at which time the attractive force became larger than the repulsive force. This observation implies that even for the gel with higher  $\nu_0$ , the domain structure could appear if the appropriate osmotic

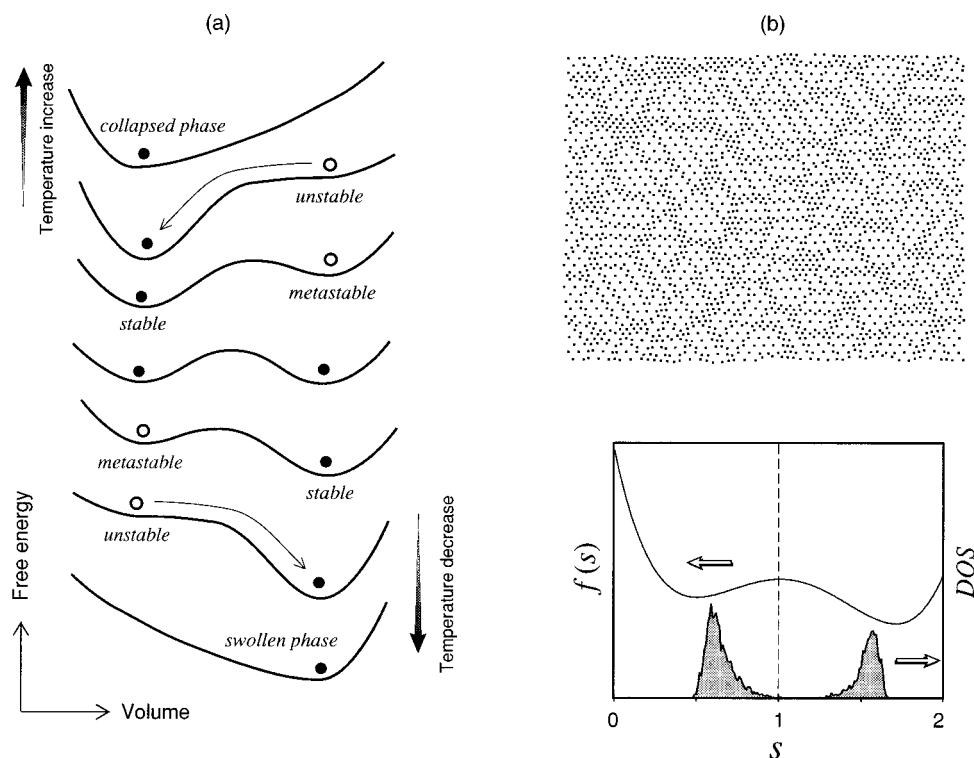


FIG. 4. Set of curves show the free energy profiles during the phase transition in NIPA gels without mechanical constraint, where the mixing free energy term is dominant (a). Under mechanical constraint, the distribution of vertex positions is determined by the mixing free energy as well as by the elastic energy on condition that the total area is constant (b). The profile of  $f(s)$  and the distribution of the relaxed  $s$  value (density of states; DOS) are illustrated.

pressure is selected. These theoretical results are qualitatively consistent with the experimental observations for the effect of the network density of poly AAM gels as well as the effect of the temperature change of poly 3BIS-NIPA gels, if the two-dimensional spongelike domains correspond to the bumps in the AFM topographies.

We have shown the qualitative explanation for the appearance of the spongelike domains with several assumptions aforementioned. The most fundamental assumptions to simplify the model should be noted as follows: First, the free energy of the system consists of two contributions of mixing free energy and the elastic energy, and second, the distribution of the initial  $\nu_0$  was mathematically given to a regular triangle for the initial state, and third, the total area of the elements was kept constant due to the mechanical constraint. As for the third assumption, it should be taken into account the recovering forces resulting from the constraint that may be proportional to the displacements of the elements. From the experimental domain size in the range from 10 to 100 nm, the element size can be estimated in the range from 1 to 10 nm, which is quite small compared with the gel thickness in the range from 10 to 50  $\mu\text{m}$ . One can say that the assumption is valid in the present simplified model and the recovering forces can be safely neglected. It could be concluded that the distribution of  $\nu_0$  as well as the configuration of  $f(s)$  are essential to determine the surface domain structures in gels, which could be enhanced by the conditions of mechanical constraint.

#### IV. SUMMARY

In this, the first reported, direct observation of the microscopic structure of polymer gel surface in a liquid by using an AFM, we observed the minute surface structure of *N*-isopropylacrylamide disk gels and poly(acrylamide) disk gels in water. The microscopic pattern formed by the domains of submicrometer scale was found on the gel surfaces, and it was strongly affected by the cross-linking density (nature of the gel network) as well as osmotic pressure (environmental condition) and thickness (condition of constraint). A theoretical simulation on the basis of a numerical model of a two-dimensional gel was presented, where the model free energy, similar to the Flory type, includes the virial term and the elastic energy. The fluctuation of the cross-linking density in the pre-gel solution at preparation was supposed to be frozen into the network structure of gels, and the local minima were sought by using the molecular dynamics method. We obtained a domainlike structure under a specific condition set. It was concluded that the gel surface can retain in the domainlike structure, if above conditions are properly selected.

We believe that the surface structure at the submicrometer level presented herein is of fundamental and technological importance in developing various applications. During the past several years, the volume of gels has been recognized to result from a balance between the repulsion and attraction of the cross-linked polymer chains in their networks.<sup>25</sup> Means of obtaining desired balance by a combi-

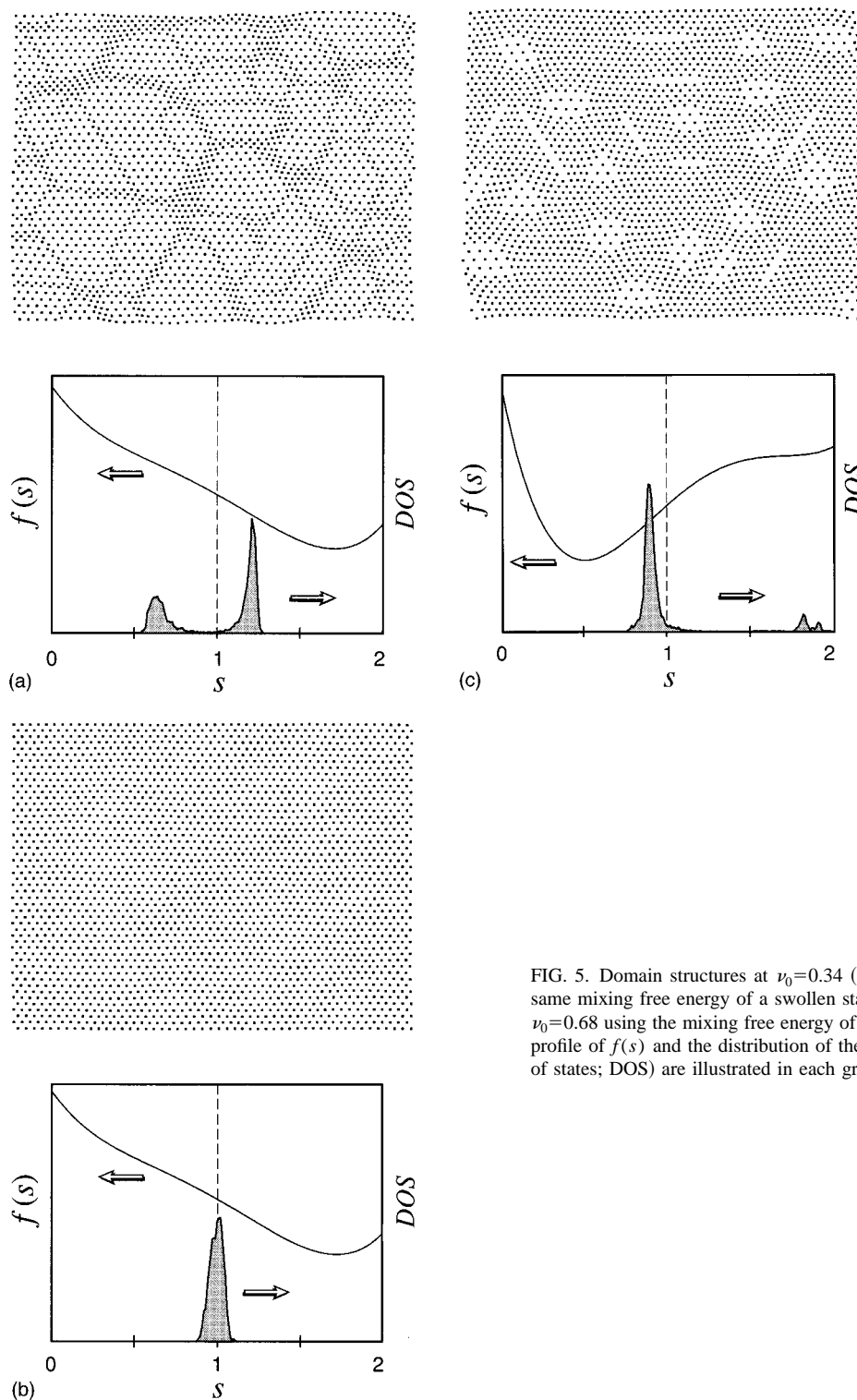


FIG. 5. Domain structures at  $\nu_0=0.34$  (a) and 0.68 (b) using the same mixing free energy of a swollen state; spongelike domain at  $\nu_0=0.68$  using the mixing free energy of a collapsed state (c). The profile of  $f(s)$  and the distribution of the relaxed  $s$  value (density of states; DOS) are illustrated in each graph.

nation of fundamental intermolecular interactions,<sup>4</sup> new phases and volume transitions between them have been discovered in some gels. By choosing appropriate monomer composition as well as the conditions, one can synthesize a gel exhibiting a unique surface structure. Control of the domain size and its nature using the external stimuli may provide new opportunities in the technology using the unique surface of gels to design the surface of heteropolymer net-

works, and it may find a variety of applications, such as sensing the environmental conditions, memorizing the surface structure, absorbing and releasing a specific molecule through intermolecular forces between the surface and the target molecule. It seems important, however, to investigate further the physical basis of the submicrometer pattern as well as the dynamic properties of the pattern formation, since the domains in this size range are an interface between the

macroscopic unique properties and nanoscopic molecular size level.

## ACKNOWLEDGMENTS

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