A perspective on auxetic nanomaterials
Harold S. Park1* and Sung Youb Kim2

Abstract
Nanomaterials have recently been found to exhibit auxetic behavior, or a negative Poisson’s ratio, whereby the lateral dimensions of the material expand, rather than shrink, in response to applied tensile loading. In this brief review, we use the form of question–answer to highlight key points and outstanding issues related to the field of auxetic nanomaterials.

Keywords: 2D materials, Auxetic, Negative Poisson’s ratio

1 What are auxetic materials and why are they of interest?
Most materials, when subject to tensile mechanical forces, elongate in the direction of the applied force, and contract in the directions normal to the applied force. This phenomenon is described mathematically by the Poisson’s ratio \( \nu \). In two-dimensions, if a material is stretched in the \( x \)-direction, it would contract in the \( y \)-direction, and its Poisson’s ratio would be defined as \( \nu_{xy} = -\epsilon_y/\epsilon_x \), where \( \epsilon \) is the strain in either the \( x \)- or \( y \)-directions. The Poisson’s ratio is typically positive because the strain normal to the applied load \( \epsilon_y \), is usually negative. Classical elasticity theory does allow for a negative Poisson’s ratio (NPR), and the Poisson’s ratio for isotropic materials can lie in the range \(-1 < \nu < 0.5 \).

Materials that expand in the lateral directions in response to an applied tensile force were termed auxetic by Evans [1]. Beginning with seminal experiments of Lakes, who demonstrated NPR in a foam structure [2], various structures and materials have been shown to exhibit the NPR phenomenon [3–15].

Auxetic materials have been widely studied for a range of target applications due to this unique mechanical property. Auxetic materials also may have enhanced shear resistance, indentation resistance, fracture toughness, and enhanced damping of wave propagation and vibration transmission in periodic auxetic structures [16, 17].

2 What mechanisms for auxetic behavior in bulk materials have been observed to hold in nanomaterials?
One of the first mechanisms for enabling auxetic behavior in bulk materials was developed by Lakes, in which a structural foam was engineering to exhibit auxetic behavior via a microstructure containing a re-entrant unit cell with two orthogonal hinges. When this structure is under mechanical tension, one of the hinges opens along the tensile axis, whereas the other hinge expands in the lateral direction, resulting in a negative Poisson’s ratio in the out-of-plane direction [2].

Interestingly, certain two-dimensional (2D) nanomaterials have an intrinsic crystal structure that precisely mimics the re-entrant hinge mechanism first utilized by Lakes. One example is black phosphorus, which has, as shown in Fig. 1, a puckered lattice structure [18], with the two hinges formed by the angles \( \theta_{546} \) and \( \theta_{214} \), thus demonstrating a nanoscale version of the re-entrant hinge mechanism.

Black phosphorus is not the only puckered two-dimensional material. Other such materials include orthorhombic arsenic [19], borophane [20], and also the monochalcogenides, like GeSe and SnS [21].

Bulk materials have also been successfully patterned through cutting techniques to induce NPR [8, 22–25], and this approach also has produced similar success in creating NPR nanomaterials. Figure 2 illustrates this for...
patterned graphene, which exhibits NPR because the internal units rotate in response to the applied strain.

3 What new mechanisms for auxetic behavior emerge at the nanoscale?
One of the distinct nanoscale effects that strongly impacts the mechanical properties of nanomaterials is the surface stress (or edge stress for 2D materials) [26, 27], which result from the fact that surface atoms have fewer bonding neighbors than atoms that lie within the material bulk. Edge buckling due to edge stresses has been found to induce NPR in narrow graphene ribbons [28], as illustrated in Fig. 3. Similarly, surface stresses have previously been shown to induce phase transformations [29], as well as shape memory and pseudoelasticity in metal nanostructures [30, 31], and were recently shown to, by
inducing phase transformations in metal nanoplates, induce auxetic behavior in the metal nanostructures, including nanoplates [32, 33] and nanowires [34].

2D nanomaterials, due to being only a single, or few atoms thick, are mechanically resistant to in-plane stretching, but can easily be induced to deform out of the 2D plane due to their small bending modulus [35, 36]. Thus, one mechanism that has been widely exploited to generate NPR in 2D materials, is that of rippling. Rippling induces NPR in 2D materials because in-plane stretching causes the ripples to flatten, and an expansion of the in-plane dimensions, resulting in a NPR.

Rippling-induced NPR has been generated in 2D materials in various ways, including thermally-induced ripples [37], introduction of 5-8-5 double vacancies in graphene [38] and hydrogenation of graphene [39]. The mechanism by which rippling induced by vacancies in graphene leads to NPR is illustrated in Fig. 4.

What are the key challenges and open issues?

There are many possibilities and challenges in the field of auxetic nanomaterials, particularly since the first report of NPR in a single-crystal nanomaterial occurred only in 2014 for both black phosphorus and metal nanoplates. One key challenge is in determining how an in-plane NPR can be induced in nanomaterials. This is because currently, essentially all examples of NPR reported so far for nanomaterials are out-of-plane, i.e. via the rippling mechanism, and also the hinge mechanism for black phosphorus. However, very few reports of in-plane NPR have emerged. For example, transition metal dichalcogenides MX$_2$ (MoSe$_2$, MoTe$_2$, WSe$_2$, WTe$_2$, TeTe$_2$, ReSe$_2$, and ReTe$_2$) shows in-plane auxeticity in the elastic range [40], and pristine graphene [41] and semi-fluorinated graphene [42] exhibit in-plane auxeticity for large tensile strains exceeding about 6 and 9%, respectively.

Another question that emerges is to move past the discovery phase of NPR in nanomaterials, and to develop a mechanistic understanding of how to controllably tune the NPR in nanomaterials, either by controllably altering the structure of nanomaterials, most likely via cutting and patterning.

Finally, most reports of NPR have so-far been in 2D materials. However, the mechanisms for NPR in 2D materials, which to-date have primarily exploited the low bending modulus to achieve an out-of-plane NPR, may not be operant for other nanomaterials, like 1D nanowires. Thus, it remains to be determined what new mechanisms can be found for other important nanomaterials.
Authors’ contributions
HSP and SYK wrote the manuscript. Both authors read and approved the final manuscript.

Author details
1 Department of Mechanical Engineering, Boston University, Boston, MA 02215, USA. 2 Department of Mechanical Engineering, Ulsan National Institute of Science and Technology, Ulsan 44919, South Korea.

Acknowledgements
HSP acknowledges helpful discussions with Prof. Jin-Wu Jiang.

Competing interests
The authors declare that they have no competing interests.

Funding
S.Y.K. acknowledges the support from the Mid-Career Researcher Support Program (Grant No. 2014R1A2A09052374) of the National Research Foundation (NRF) of Korea.

Publisher’s Note
Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Received: 4 February 2017 Accepted: 7 April 2017 Published online: 16 April 2017

References
1. K.E. Evans, Endeavour 15(4), 170 (1991)
2. R.S. Lakes, Science 235, 1038 (1987)
3. L. Rothenburg, A.A. Berlint, R.J. Bathurst, Nature 354, 470 (1991)
4. R. Lakes, Adv. Mater. 5, 293 (1993)
5. R.H. Baughman, D.S. Galvao, Nature 365, 735 (1993)
6. K.E. Evans, A. Alderson, Adv. Mater. 12(9), 617 (2000)
7. W. Yang, Z.M. Li, W. Shi, B.H. Xie, M.B. Yang, J. Mater. Sci. 39, 3269 (2004)
8. N. Ravirala, A. Alderson, K.L. Alderson, J. Mater. Sci. 42, 7433 (2007)
9. Z.A. Lethbridge, R.I. Walton, A.S. Marmier, C.W. Smith, K.E. Evans, Acta Mater. 58, 6444 (2010)
10. K. Bertoldi, P.M. Reis, S. Willshaw, T. Mullin, Adv. Mater. 22, 361 (2010)
11. K. Alderson, A. Alderson, S. Anand, Y. Simkins, S. Nazare, N. Ravirala, Phys. Status Solidi B 249(7), 1322 (2012)
12. A. Clausen, F. Wang, J.S. Jensen, C. Sigdem, J.A. Lewis, Adv. Mater. 27, 5523 (2015)
13. F. Milestein, K. Huang, Phys. Rev. B 19(4), 2030 (1979)
14. R.H. Baughman, J.M. Shacklette, A.A. Zakhidov, S. Stafstrom, Nature 392, 362 (1998)
15. J.W. Jiang, S.Y. Kim, H.S. Park, Appl. Phys. Rev. 3, 041101 (2016)
16. K.K. Saxena, R. Das, E.P. Callus, Adv. Eng. Mater. 18(11), 1847 (2016)
17. C. Huang, L. Chen, Adv. Mater. 28, 8079 (2016)
18. J.W. Jiang, H.S. Park, Nat. Commun. 5, 4727 (2014)
19. J. Han, J. Xie, Z. Zhang, D. Yang, M. Si, D. Xue, Appl. Phys. Expr. 8(4), 041801 (2015)
20. L. Kou, Y. Ma, C. Tang, Z. Sun, A. Du, C. Chen, Nano Lett. 16(12), 7910 (2016)
21. P.Z. Hanakata, A. Carvalho, D.K. Campbell, H.S. Park, Phys. Rev. B 94, 035304 (2016)
22. J.N. Grima, K.E. Evans, J. Mater. Sci. Lett. 19, 1563 (2000)
23. C.W. Smith, J.N. Grima, K.E. Evans, Acta Mater. 48, 4349 (2000)
24. N. Gaspar, X. Ren, C. Smith, J. Grima, K. Evans, Acta Mater. 53, 2439 (2005)
25. J.N. Grima, K. Evans, J. Mater. Sci. 41, 3193 (2006)
26. R.C. Cammarata, Prog. Surf. Sci. 46(1), 1 (1994)
27. W. Haiss, Rep. Prog. Phys. 64, 591 (2001)
28. J.W. Jiang, H.S. Park, Nano Lett. 16, 2667 (2016)
29. J. Diao, K. Gall, M.L. Dunn, Nat. Mater. 2, 656 (2003)
30. H.S. Park, K. Gall, J.A. Zimmerman, Phys. Rev. Lett. 95(25), 255504 (2005)
31. W. Liang, M. Zhou, F. Ke, Nano Lett. 5(10), 2039 (2005)
32. D.T. Ho, S.D. Park, S.Y. Kwon, K. Park, S.Y. Kim, Nat. Commun. 5, 3255 (2014)
33. D.T. Ho, H. Kim, S.Y. Kwon, S.Y. Kim, Phys. Status Solidi B 252(7), 1492 (2015)
34. D.T. Ho, S.Y. Kwon, S.Y. Kim, Sci. Rep. 6, 27560 (2016)
35. Q. Lu, M. Arroyo, R. Huang, J. Phys. D. 42, 102002 (2009)
36. J.W. Jiang, Z. Qi, H.S. Park, T. Rabczuk, Nanotechnology 24, 435705 (2013)
37. K.V. Zakharchenko, M.I. Katsnelson, A. Fasolino, Phys. Rev. Lett. 102(4), 046808 (2009)
38. J.N. Grima, S. Winczewski, L. Mizzi, M.C. Grech, R. Cauchi, R. Gatt, D. Attard, K.W. Wojciechowski, J. Rybicki, Adv. Mater. 27, 1455 (2015)
39. J.W. Jiang, T. Chang, X. Guo, Nanoscale 8, 15948 (2016)
40. L. Yu, Q. Yan, A. Ruzsinszky, https://arxiv.org/abs/1701.06529 (2017)
41. J.W. Jiang, T. Chang, X. Guo, H.S. Park, Nano Lett. 16, 5286 (2016)
42. R. Qin, J. Zheng, W. Zhu, Nanoscale 9, 128 (2017)
43. V.H. Ho, D.T. Ho, S.Y. Kwon, S.Y. Kim, Phys. Status Solidi B 253(7), 1303 (2016)