Reply to the Comment on "Reevaluation in Interpretation of Hydrophobicity by Scaled Particle Theory"

Masato Kodaka*

Institute of Molecular and Cell Biology, National Institute of Advanced Industrial Science and Technology (AIST), Central 6, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8566, Japan

I am grateful to Graziano for his comment on the paper. I would like to show, however, that the comment by Graziano is based on an incorrect understanding of the paper. The important point in the paper is that the curves shown in Figures 2 and 3 are those of nonpolar or weakly polar liquids and are regarded as standard curves. I never state in the paper that eq 7 can be applied to water because eq 7 is derived only for nonpolar or weakly polar liquids to obtain the standard relationship between the packing density (y) and the hard-sphere diameter of solvent molecules (a_1). The fundamental strategy of the present study is to interpret hydrophobicity by analyzing the deviation of water from standard behavior. Therefore, if water were a nonpolar or weakly polar liquid, the data of water would be situated near the curves corresponding to the ordinary liquids (types b or c) in Figure 2. The result that the y value of water is larger than that expected for ordinary liquids of the same size (Figure 2) shows that there should be some effects that increase the number density (ρ) in water. In the case of water, the larger ρ value is mainly attributed to the large cohesive energy density (ced) due to hydrogen bonding. The contribution from internal pressure to its p value must be small because the real internal pressure of water is small. In this respect, I clearly state in the paper that water has a real internal pressure (1.7×10^8 Pa) that is smaller than the P_{int} value (7.4×10^8 Pa) obtained from eq 7. Furthermore, it should be noted that P_{int} obtained from eq 7 is regarded as the apparent internal pressure in water, hydrazine, and ethylene glycol, as mentioned in the paper.

Next, I would like to reply to the four points mentioned by Graziano. With respect to the first point, it is not mentioned in the paper that P_{int} is independent of a_1 in all liquids. Figure 1 shows that P_{int} is independent of a_1 only in a homogeneous series of nonpolar liquids. Namely, I never show that this result can be applied to water. The result in Figure 1 is used to obtain only the standard relationship for nonpolar or weakly polar liquids in Figures 2 and 3. Therefore, the first point suggested by Graziano is not proper. With respect to the second point, I do not assume that $P_{int} \cong ced$ for all liquids. It should be noted that $P_{int}(\exp) \cong ced$ in eq 6 is used only for Figure 1, in which the relation between $P_{int}(\exp)$ and a_1 is given for cycloalkanes. It is clearly described in the paper that eq 6 holds only for weakly polar liquids. Thus, the second point suggested by Graziano is also not correct. With respect to the third point, I show that eq 5 holds only for weakly polar liquids. Therefore, Graziano's third comment is incorrect. With respect to the fourth point, it should be noted again that the curves in Figure 2 show the standard relation between y and a_1 for liquids without strong molecular interactions. Obviously, the y value for water is much larger than that expected for standard liquids with the same size. The only possible mechanism to increase the y value (that is, the p value) should be the strong molecular interactions caused by hydrogen bonding. To draw this conclusion, there is no need to assume that $P_h \cong P_{int} \cong ced$ for water.

In conclusion, hydrophobicity is caused by the high packing density of water, which is due to strong molecular interactions caused by hydrogen bonding.

* E-mail: m.kodaka@aist.go.jp.