Particulate Pictures and Kinetic-Molecular Theory Concepts: Seizing an Opportunity

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While quantitative and mathematical problem solving remains at the center of introductory college chemistry, there has been an increasing use of conceptual approaches to understanding basic chemical phenomena at the microscopic or particulate level. This particulate approach has also made its way into the physical science curriculum, typically beginning in the middle grades. There is a significant body of work that investigates the effects of these different conceptions on student learning at the undergraduate level (1–16). A survey of textbooks from the middle grades (17–19) through general chemistry (20) shows similar figures under similar conditions to those in the assessment questions frequently cited in learning studies (6, 10). While these pictures and assessment questions have led to a better understanding of student learning resulting from differing pedagogical approaches, they have some substantial flaws. Significant misconceptions are inherent in the representations (e.g., lack of motion, see ref 12) or often incorporated into the illustrations used (e.g., scale). Specifically, the images used often misrepresent the particulate nature of a gas relative to that of solid or liquid. The relative distances between particles for the different states of matter has been specifically identified by others as one of the student misconceptions in the middle to high school grades (21, 22). When coupled with the lack of motion indicated in many of these figures, there is a risk of building and solidifying common student misconceptions about the nature of matter and the kinetic-molecular theory (see refs 2, 23 and references cited in 3). An additional ambiguity exists in the apparent container cross sections shown in some of these figures (see Figure 1 discussed in text below). For example, is this a slice through the tank, a magnified region[1] within the tank, or a projection of a 3-D tank into 2-D space? While the descriptions or the images themselves might be altered to better reflect the reality of a gas compared to the condensed phase, I make the case that these representations offer a "teachable moment" regarding the nature and limitations inherent in models, as well as an opportunity for students to critique and develop model figures that better fit the physical conditions.

In addition, the general lack of precision used in the development of figures of this type may have an impact on K–12 teachers, as illustrated by studies of particulate understanding among teachers (2). As Gabel, Samuel, and Hunn point out (2):

> [T]he careful representation of particles by chemists when they are used in instruction might bring about not only an increased ability to solve chemistry problems but it may also help to make chemistry more understandable by providing the framework underlying the discipline.

Though a range of questions, both qualitative and more quantitative, are often asked along with pictures that are close and not-so-close to the reality described, the question and pictures to be specifically discussed here are illustrated in Figure 1 (6, 13).

This question is chosen because of its continued wide use in the literature examining conceptual learning and problem-solving abilities of students taught using various pedagogical tools (1–16). It also mirrors figures seen throughout textbooks and assessments for middle grades through the undergraduate level. Both versions of the pictures are used as they show some clear differences.

Analysis of the Particulate Pictures

To begin an inquiry into the representations shown, one might start with a key postulate from the kinetic-molecular theory of gases: *the distance between particles is much larger than the particles themselves*. Obviously there is the potential limitation in any such model that atoms and molecules are extremely small. For example, when illustrating basic atomic structure, it is not possible on a normal page to accurately represent the relative size of the nucleus compared to the atom (i.e., 5 orders of magnitude difference in radius). However, in the case of the particulate pictures of gases, the scale can be accurately represented because the sizes of the particles and the distances between them are not so vastly different.

Using the van der Waals equation of state, the percentage of the volume occupied for hydrogen gas at 20 °C and 3 atm is 0.33%. From the van der Waals b parameter, the effective radius of hydrogen is calculated to be 2.19×10^{-10} m. The radius of a container, with height equal to 1 molecular diameter, necessary for 0.33% volume particle occupation (at 293 K and 3 atm) was determined. The radii of hydrogen and the container were used to determine an apparent percentage of the area occupied for a two-dimensional container view (see Table 1). To compare to the figures of Nurrenbern and Pickering (6), and Sanger and Phelps (13), their two-dimensional figures were translated to three dimensions, assuming spherical molecules and a cylindrical container, and the relative volumes were calculated. Because the figures were specified as cross sections, it was assumed that they represent a cylinder that is 1 particle diameter in height. While the figures show 5.9–17% area occupation, the prediction using the van der Waals equation of state for hydrogen, under the specified conditions, gives the occupation as only 0.49% by area. The error in the apparent volume occupation in these pictures is 6–17 times that predicted by theory.

When moving from the qualitative particulate view (e.g., which figure is most consistent with a gas?) to a more quantitative view (e.g., associating figures with particular values of T and P), one must be especially cognizant of the role that the motion of the particles plays. In fact, Sanger et al. (12) have identified the lack of motion in the figures as one potential threat

The following diagram represents a cross-sectional area of a steel tank filled with hydrogen gas at 20 °C and 3 atm pressure. (The dots represent the distribution of H_2 molecules.)
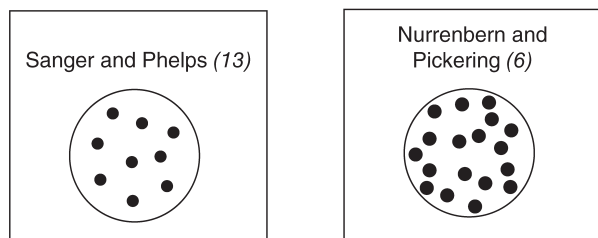
Which of the following diagrams illustrate the distribution of H_2 molecules in the steel tank if the temperature is lowered to −20 °C?
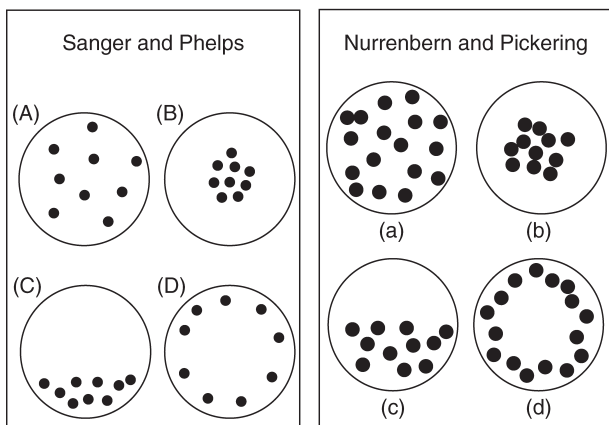

Figure 1. The conceptual understanding assessment question as stated and illustrated in refs 6 and 13.

Table 1. Apparent and Predicted Space Occupation for Particles of Hydrogen at 20 °C and 3 Atm

Source	Area Occupied, %	Volume Occupied, %
van der Waals	0.49	0.33
Sanger (13)	5.9	4.0
Nurrenbern and Pickering (6)	17	12

to the question's validity and examined the role that animation of the particles in these assessment questions played in student learning outcomes.

Though mentioned in some general chemistry texts (24), it is typically not until physical chemistry that students are introduced to the concept of mean free path. The estimate of this average distance between collisions is readily derived from kinetic-molecular theory.

The mean free path predicted for hydrogen at 20 °C and 3 atm would be 3.49×10^{-8} m. This distance is 80 times the effective molecular diameter of hydrogen (4.38×10^{-10} m). While much less than the 5 orders of magnitude difference between nuclear and atomic radii, it would seem that 2 orders of magnitude difference in size might still limit the ability to accurately indicate scale in these pictures. However, the mean free path is not an accurate measure of the average distance between particles (25). Consideration of the average particle

Table 2. Average Separation of Particles of Hydrogen at 20 °C and 3 Atm

Source	Apparent Average Molecular Separation, Particle Diameters
Nurrenbern and Pickering (6)	2.3
Sanger (13)	3.4
	Average Molecular Separation, Particle Diameters (T = 20 °C, P = 3 Atm)
Kinetic-molecular theory	5.4

Table 3. Pressure To Achieve Apparent Average Separation in Figures at 20 °C

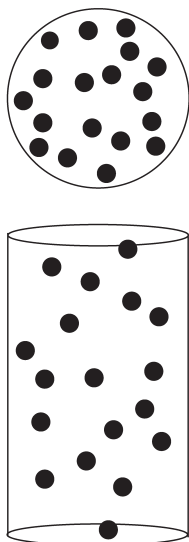| Source	Apparent Pressure, Atm
Nurrenbern and Pickering (6)	104.0
Sanger (13)	35.8

separation in a gaseous sample is frequently neglected in physical chemistry texts, but might be important if one were to accurately represent a gas using these particulate figures. A simple estimate of this average particle separation can be made based on the volume of the container and the number of particles in the sample (26): the mean particle separation is equal to the cube root of V/N, where V is the volume of the container (assumed cubic for simplicity) and N is the total number of particles in the container.

Using this approximation, the average molecular separation for hydrogen gas at 20 °C and 3 atm is 2.37×10^{-9} m or 5.4 molecular diameters. Using this consideration, the figures of focus here differ from prediction, with the distances between particles 1.6−2.4 times less than this (see Table 2). Alternatively, one can start with the figures shown and calculate the pressure (or temperature) required to reach these average particle separations. As shown in Table 3, these pressures are 12−35 times the 3 atm pressure cited in the text of the question. Further, the apparent particle separations are significantly underestimated because only the two-dimensional measurement of distances in the pictures is considered. If one moves to three-dimensional measurements, considering the relative positions of particles in the adjacent cross sections in the tank, the average separations would be less than that presented in the two-dimensional pictures (see discussion below).

Issues of Phase Representation

Omitted from the statement of the question is the boiling point of hydrogen at 3 atm. Without that information, or knowledge of boiling points for similar gases, students would not be able to judge whether condensation of the gaseous hydrogen is likely or unlikely to occur when decreasing the temperature to −20 °C (6). Sanger et al. cite this misidentification of the conditions under which changes in state occur as one threat to the question's validity (12). Using the normal boiling point (20 K) and the enthalpy of vaporization (0.90 kJ/mol) (27, 28), the Clausius−Clapeyron equation predicts the boiling point of hydrogen at 3 atm to be 25.8 K (−247 °C). While a student choosing a response consistent with a condensed phase (e.g., choice C) would be in error by nearly an order of magnitude in absolute temperature, the error is similar to the factor of

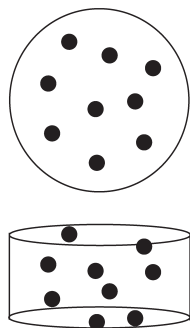Nurrenbern and Pickering *(6)*   Sanger and Phelps *(13)*

Figure 2. Representation of the tank size necessary to reach the cited conditions with the number and size of particles represented in the original figures.

12−35 times in the apparent pressure in the figure as compared to the stated pressure in the question. However, it is generally easier to experimentally achieve a 10-fold increase in pressure than to achieve a 10-fold decrease in absolute temperature, such that the error in absolute temperature might be considered more significant.

The critical point for hydrogen is 33 K and 13 atm; thus, the figures under discussion here are actually more consistent with supercritical hydrogen. In both cases, the temperature is 293 K and the pressure is 17.9 atm *(12)* or 52 atm *(6)*.

Perspective of the Container

Another potential way to view figures of the type described here would be as projections of a cylindrical tank into two-dimensional space, from which the size of the tank can be estimated. Figure 2 illustrates the relative tank sizes that would lead to the van der Waals predicted value of 0.33% volume occupation for hydrogen gas at 20 °C and 3 atm. In each case, the tank is shown with the same total number of particles that are specified for the "cross section" of the tank in the original question.

Corrected Representation of Particulate Picture

To more accurately represent hydrogen molecules at 20 °C and 3 atm, scaling of the particle size and container size must be done. Assuming a cross section of a cylindrical tank that is 1 molecular diameter in height, one would predict the representation shown in Figure 3. The figure was scaled from particles that were 13 mm in diameter and a container that was 3.68 cm in diameter.

Measurement of the relative positions of the particles shows that the apparent average particle distance is 13 particle diameters, which is significantly greater than the 5.4 particle diameters predicted by kinetic-molecular theory (see Table 2). While a portion of this discrepancy might be attributed to the small number of measurements, this is more completely addressed by the fact that we are only looking at a single cross section, rather than the bulk of the
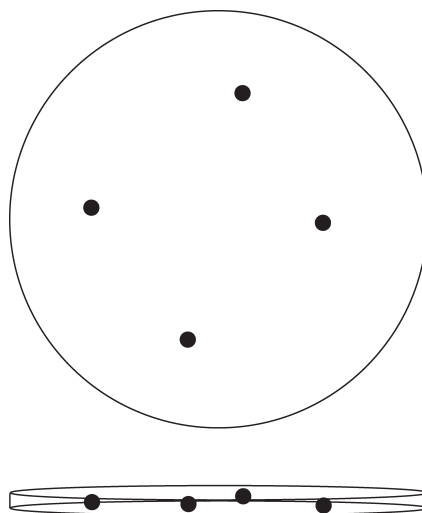

Figure 3. An improved model for illustration of hydrogen at 20 °C and 3 atm in which the cross section represents a cylinder that is 1 particle diameter in height.

Figure 4. Visualization of adjacent cross sections of the tank. Particles in the upper and lower cross section are shaded for clarity.

gas sample. This is analogous to the difficulty in visualizing the coordination number of six for an atom in a simple cubic lattice when looking at a picture of a single unit cell. In that case, the key is to envision the wider lattice, rather than a single unit cell. A very similar idea may be used here. By including the adjacent cross sections of the tank, one can see that additional nearest neighbors are "introduced" into consideration (see Figure 4).

The picture of Figure 3 represents more accurately the nature of hydrogen gas under the stated conditions, but it may also be adapted easily to other conditions. Using the same scale, decreasing the number of particles to 1 would reduce the pressure to 0.75 atm, while increasing the number to 18 would take the pressure to 13.5 atm (just above the critical pressure of 13 atm). Alternatively, the picture in Figure 3 would also be consistent with a pressure of 1 atm at 98 K; under these conditions, one could increase the number of particles to 52 before reaching the critical pressure.

Though widely used, and granting that much has been discovered about conceptual learning based on the figures and question discussed, the representations themselves have a serious flaw. These same shortcomings are ubiquitous in textbooks and assessments from the middle grades through the undergraduate level. While printed figures are not able to accurately represent the motion of the particles (directionally random with a Maxwell−Boltzmann distribution of speeds), they can easily be produced with at least proper scale. This at least allows an accurate representation of the large distance between gas particles.

Some Classroom Uses for Particulate Pictures

Whether correct in their representations or not, these pictures offer educators an opportunity for a variety of exercises

aimed at a greater inquiry into the kinetic-molecular theory and the representation of scale. For example, students might be given a figure and asked to critique it (e.g., with respect to scale, apparent pressure, lack of motion). At the introductory or general chemistry level, one could specify the container height and ask students to determine the apparent pressure. Taking this a step further, one could give students a phase diagram (or simply some relevant points on the diagram) and ask students to specify the phase of substance illustrated by a particular figure at a specified temperature.

A more open-ended activity would be to have the students develop their own particulate drawings. The guidelines would be that the container and particles should be drawn to scale, to best represent a particular gas at a given temperature and pressure. This would perhaps be best done after coverage of the van der Waals equation of state, though the students would need to realize the need for and usefulness of the b parameter for the exercise. If left open-ended, students would need to make a choice on the container shape and dimensions. This could be used to lead students to the concept of the average particle separation in a gas, which could be contrasted with the mean free path.

Another exercise could have students examine scale by providing them with the radius of the gas particles, the temperature, pressure, and number of particles, and then determining the size of the container necessary. Students in a physical chemistry course could be asked to go deeper and develop a picture, given a set of conditions and the size of the particles. Students could then be asked to explain why the distance between particles in Figure 3 is so much less than the mean free path. Students could then move to the next step in calculating the average distance between particles in a gas, introducing this concept into the physical chemistry curriculum. Finally, students could be asked to explain why the distances between particles in Figure 3 are significantly larger than the prediction for the average particle separation. The explanation could be linked back to the spatial conceptions inherent in understanding basic crystal structures from general chemistry.

In summary, even within the limitations of static pictures, we can and should provide meaningful particulate-level pictures of gases for students. These pictures might be used in place of those found currently in textbooks and assessment tools. In addition to better pictures to present or assess conceptual content knowledge of gases, a better understanding of spatial relationships at the quantitative level can be addressed at the level of a physical chemistry course (e.g., mean free path vs average particle separation). While professional chemists may tend to conceptualize both the macroscopic and microscopic views of nature (29), the typical student and many teaching science may not yet be at this level of comfort, which suggests that additional care and precision should be used when illustrating the particulate world in our texts and assessment tools.

Acknowledgment

Note

1. By "magnified region" I mean that the boundary represented by the circle would be the field of view for the magnifying device,

rather than the walls of the container. A number of textbooks present figures that incorporate photographs with added artwork indicating a magnified region of the substance in the container shown (19, 20).

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