The role of the electronic subsystem in phase transitions

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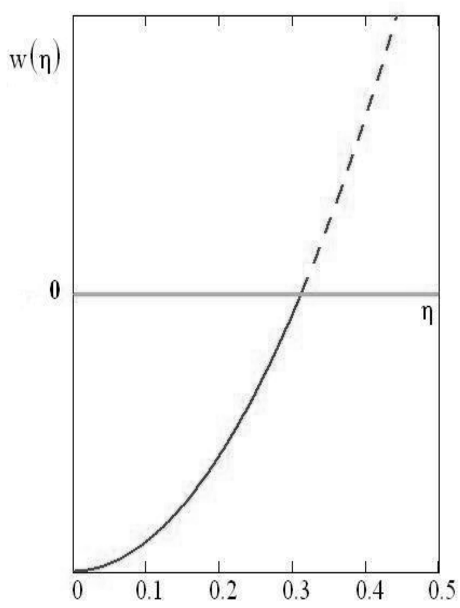
When considering phase transitions between the basic aggregate states of a substance, phenomenological considerations are usually used. It is based on the application of the order parameter. For phase transitions from liquids to gases such a phenomenological consideration is permissible. But when considering crystal-liquid transitions, it is impossible to ignore the quantum nature of interatomic interactions. The sequential (in the quantum sense) allowance for the electronic subsystem makes it possible to clarify not only the physical nature of the crystal-liquid and liquid-gas transitions, but also to clarify the physical entity of the order parameter.

The internal energy of an ideal monatomic crystal is analyzed. For example, diamond, graphite, graphene, fullerenes, nanotubes and even proteins. It is shown that the specific internal nanoenergy (per one atom) has the form:

$$w(\eta) = -\left[U_S^{(0)} + U_A^{(0)}\right] + \left[U_S^{(1)} + U_A^{(1)}\right]\eta(T) + \left[U_S^{(2)} + U_A^{(2)}\right]\eta^2(T). \tag{1}$$

In this energy, the η factor is a direct analog of the order parameter. But here it has a precise definition: $\eta(T) \equiv \left(1 + \exp\left(E_{\mathrm{g}}/2kT\right)\right)^{-1}$, where E_{g} is the width of the forbidden band. It describes the effect of an external thermostat on the specific internal energy of the condensate. The Fermi factor $\eta(T)$, with increasing temperature in the region $0 \le T < \infty$, increases within the range $0 \le \eta(T) < 1/2$. It can be considered as an overdetermined temperature. The rectangular brackets in the energy (1) contain two types of interactions. First, it is the energies $U_S^{(0)}$, $U_S^{(1)}$ and $U_S^{(2)}$. They consist only of centrally symmetric matrix elements. These are quantum-averaged energies of the interaction of electrons with nuclei and with each other. They determine only the isotropic coupling between atoms, which is characteristic of liquids. In the far-zone approximation, they have a Coulomb asymptotic behavior and are reduced to a combination of factors: $1/R$, where R is the distance between neighboring atoms. Secondly, these are energies $U_A^{(0)}$, $U_A^{(1)}$ and $U_A^{(2)}$. They contain only centrally non-symmetric matrix elements. These are quantum-averaged energies of the so-called exchange interaction. They determine only the anisotropic coupling between atoms, singling out crystallographic directions. In the far-zone approximation, they consist of combinations of factors of the form: $\varphi_f(-\mathbf{R})\varphi_g(\mathbf{R})/R$. The factors $\varphi_f(\mathbf{R})$, $\varphi_g(\mathbf{R})$, are the wave functions of the one-electron ion (here carbon, oxygen, nitrogen or hydrogen) for the valence band $(\{f,g\} = v)$ or conduction band $(\{f,g\} = c)$. In the energy (1) for condensates of the carbon series in the crystallographic directions, the condition is always satisfied: $\left[U_S^{(0)} + U_A^{(0)}\right] > 0$. This means that at zero temperature ($\eta = 0$) the energy (1) is negative. I.e. it corresponds to the bound state. In (1), for the condensates of the carbon series, the following condition is always satisfied: $\left[U_S^{(2)} + U_A^{(2)}\right] > 0$, i.e. with increasing temperature this summand uniquely provides an increase of energy. As for the summand linear on $\eta(T)$ in (1), the factor $\left[U_S^{(1)} + U_A^{(1)}\right]$ can be either positive or negative, but this factor is small. Therefore for definiteness the situation $\left[U_S^{(1)} + U_A^{(1)}\right] > 0$ is illustrated here.



The figure shows the qualitative form of the dependence $w(\eta)$. The intersection point of the curve $w(\eta)$ and the η axis (condition: $w(\eta)=0$) determines the liquid-gas transition point and the value of the parameter η, as well as the corresponding phase-transition temperature. The crystal-liquid transition is due to absence of crystallinity of the structure of the condensate. Therefore, it connected with the absence of anisotropic contributions to interatomic interactions. That is the crystal-liquid transition is determined by the condition: $-U_A^{(0)}+U_A^{(1)}\eta+U_A^{(2)}\eta^2=0$. This condition gives a temperature value less than value determined by the condition $w(\eta)=0$.